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A MODEL TO PREDICT THE EFFECTS OF AIR-WATER GAS EXCHANGE ON LINDANE CONCENTRATIONS IN LAKE ONTARIO

by

Alexandra Stuart Relph

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Graduate Department of Mechanical and Industrial Engineering
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Abstract

A Model to Predict the Effects of Air-Water Gas Exchange on Lindane Concentrations in Lake Ontario

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1998

DYRESM, a one-dimensional model that predicts the vertical temperature distribution in lakes, was modified to include concentrations of soluble chemicals resulting from air-water gas transfer. The new model was applied to Lake Ontario to determine concentrations of the pesticide Lindane for several scenarios over one to four year periods. Air-water gas exchange was found to be a dominant process affecting Lindane concentration in Lake Ontario. Lindane's solubility was the most important factor for determining the direction of gas flux. Predictions from a baseline simulation for the International Field Year on the Great Lakes (1972-1973) were similar to measured concentrations of approximately 0.4 $ng L^{-1}$ during the summer months and 0.3 $ng L^{-1}$ during the winter. Lindane was determined to be deposited by air-water gas exchange in spring and summer, and volatilized in autumn and winter, with a net annual deposit to Lake Ontario.
Acknowledgements

I'd like to thank my supervisor, Professor Mark Loewen, for his guidance and patience. Also, I must extend my appreciation to Dr. Paul Hamblin at the Canadian Centre for Inland Waters, who provided our Lake Ontario data and version of DYRESM.

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The other folks who made it fun: Claire, Kath, Pier, Marc, Cesar, El, Nat, the new lab kids, the Sunnybrook gang, Fresh Baked Buns, Hammered Penguins, team Virgo, the rest of the TUC, AMIGAS and friends, McGill types, and of course... Torontula rules!

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DYRESM was created by Imberger and Patterson at the Centre for Water Research at the University of Western Australia.
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Nomenclature

- $A_i$: surface area of $i^{th}$ layer ($m^2$)
- $B$: lake width ($m$)
- $C$: wind sheltering coefficient
- $C_a$: concentration in air ($kg \ m^3$)
- $C_d$: drag coefficient
- $C_H$: bulk transfer coefficient for heat
- $C_k$: stirring efficiency coefficient
- $C_m$: centre of mass of stratified layers ($m$)
- $C_mm$: centre of mass of mixed layer ($m$)
- $C_p$: specific heat of water
- $C_s$: shear production efficiency coefficient
- $C_t$: coefficient for unsteady effects
- $C_w$: concentration in water ($kg \ m^3$)
- $C_{W}$: bulk transfer coefficient for moisture
- $D_a$: diffusivity in air ($m^2 \ s^{-1}$)
- $D_w$: diffusivity in water ($m^2 \ s^{-1}$)
- $E$: evaporative heat flux ($J \ m^{-2} \ s^{-1}$)
- $E_{ac}$: energy available from convective cooling
- $E_{ap}$: energy available from shear production
- $E_{as}$: energy available from stirring and convective overturn
- $E_{inflow}$: power input from inflowing rivers
- $E_r$: energy required to entrain layers below the thermocline
- $E_{wind}$: power input due to wind stirring at the surface
- $F$: rate of transfer through surface of lake ($kg \ m^{-2} \ s^{-1}$)
- $F_i$: Froude number of inflow
- $F_o$: Froude number of outflow
- $Gr$: Grashof number
- $H$: dimensionless Henry's law constant
- $H_L$: depth of the lake ($m$)
- $H_s$: depth of surface layer ($m$)
- $\dot{H}$: conductive heat flux ($J \ m^{-2} \ s^{-1}$)
- $K_a$: transfer velocity in air ($m \ s^{-1}$)
- $K_w$: transfer velocity in water ($m \ s^{-1}$)
- $K_{tot}$: total gas transfer velocity ($m \ s^{-1}$)
\( L \) reservoir depth \((m)\)
\( N \) Brunt-Vaisala frequency
\( P \) gas phase pressure \((atm)\)
\( P_s \) potential energy of stratified lake
\( Q \) rate of river inflow or outflow \((m^3 \text{ s}^{-1})\)
\( Q_{AC} \) long-wave radiation absorbed
\( Q_n \) total radiation intensity at each layer's surface
\( Q_s \) short-wave radiation intensity
\( Q_W \) long-wave radiation emitted
\( R \) non-dimensional number combining \( F_i \) and \( Gr \)
\( S_{ca} \) Schmidt number in air
\( S_{cw} \) Schmidt number in water
\( T \) temperature \((^\circ C \text{ or } ^\circ K)\)
\( T_d \) damping period of lake \((s)\)
\( T_i \) wave period of lake \((s)\)
\( T_m \) mixing time scale \((s)\)
\( U \) wind speed \((m \text{ s}^{-1})\)
\( U_{aw} \) average shear velocity \((m \text{ s}^{-1})\)
\( \Delta U \) mean velocity shear from horizontal internal wave motions \((m \text{ s}^{-1})\)
\( V_a \) molecular volume of air \((cm \text{ mol}^{-1})\)
\( dV_H \) volume of water removed by outflow \((m^3)\)
\( dV_i \) volume of water added by inflow \((m^3)\)
\( V_L \) molecular volume of Lindane \((cm \text{ mol}^{-1})\)
\( V_{max} \) maximum layer volume \((m^3)\)
\( V_{min} \) minimum layer volume \((m^3)\)
\( W \) Wedderburn number

\( d_i \) height of \( i^{th} \) layer \((m)\)
\( e \) intrusion length of inflowing river \((m)\)
\( f \) Coriolis parameter
\( g \) gravity \((m \text{ s}^{-2})\)
\( g' \) effective reduced gravity \((m \text{ s}^{-2})\)
\( h \) depth of the mixed layer \((h)\)
\( h_o \) initial flowing depth \((m)\)
\( m_a \) molecular mass of air \((g \text{ mol}^{-1})\)
\( m_L \) molecular mass of Lindane \((g \text{ mol}^{-1})\)
<table>
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<td>$t_{eff}$</td>
<td>effective cut-off time for wave motion</td>
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<tr>
<td>$\Delta t$</td>
<td>time step ($s$ or $min$)</td>
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<td>$u_{max}$</td>
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<tr>
<td>$u_*$</td>
<td>friction velocity at surface</td>
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<td>half angle of river bottom</td>
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<td>convective and stirring parameter</td>
</tr>
<tr>
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<td>viscosity (centipoise)</td>
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<tr>
<td>$\phi$</td>
<td>slope of the river bed</td>
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<tr>
<td>$\rho$</td>
<td>density ($kg m^3$)</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stephan-Boltzman constant</td>
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Chapter 1

Introduction

The atmosphere is known to be a major source of synthetic organic chemicals to the Great Lakes [29, 46]. For persistent, highly soluble organochlorine pesticides such as Lindane (γ-HCH), the primary pathway into the surface waters of large lakes is air-water gas transfer [2, 33, 43]. This includes volatilization from the water into the atmosphere and absorption into water from the air. Other mechanisms of chemical exchange, including wet and dry deposition, have been found to be much less important for this ubiquitous chemical [16, 35].

The methods of transport of chemicals in an aquatic ecosystem are influenced by the compound’s properties and environmental factors. Consequently, the task of modelling chemical transport and fate is a difficult one. Mackay [28, 32] has performed extensive analyses of the partitioning of chemicals between media in a lake system, including the effects of uptake by biota, sedimentary deposition, and chemical degradation. However, for Lindane, it is well established that air-water gas transfer is the dominant process [2, 16].

Lindane is the most abundant chlorinated hydrocarbon in the earth’s atmosphere and surface waters [24]. It is transported globally in the atmosphere, often over long ranges, and is highly persistent [47]. Although not presently in use in North America, Lindane has been produced since the second world war and is still used as an agricultural pesticide in many countries [29]. It is of particular interest in the study of air-water gas transfer because it is widely used, persistent, has high concentrations in the air and lakes, and does not attach easily to particulate matter [16, 24].

Air-water gas exchange is a dynamic, cyclical process between the atmosphere and water bodies. For soluble chemicals such as Lindane, this flux is thought to be primarily depositional with seasonal variations [44]. These variations are expected to occur because lakes are near chemical equilibrium; since a chemical’s solubility is dependent on temper-
nature, daily weather conditions directly affect the amount of chemical absorbed into the surface waters [19]. Baker and Eisenreich [2] have theorized that while mechanisms such as wet deposition may provide large-scale, instantaneous inputs to a lake, gas exchange across the air-water interface is prolonged and has an overall greater impact.

For highly soluble compounds, gas transfer is primarily diffusive and is governed by wind speed, air temperature, water temperature, and the solubility of the chemical. The overall flux is characterized by a gas transfer velocity, determined from the meteorological conditions and chemical properties [46]. More severe weather conditions tend to increase the rate at which chemicals are exchanged between the two media. Gases which are less soluble may experience an additional contribution to the gas transfer velocity from storm-induced bubbles, but these effects are negligible for Lindane [13].

Inclusion of surface gas exchange processes in models of lakes has been performed for dissolved oxygen, PCBs and other compounds [2, 8]. However, most of these models have focused on the flux through the surface waters, and not on the lake-wide concentration resulting from surface chemical inputs. Mackay et al. [31, 33] have provided generalized analytical results for the partitioning of a number of chemicals between media in lakes, but have not examined lake mechanics exhaustively. The goal of this research was to combine an algorithm for air-water gas transfer developed by Hancock [13] with a comprehensive model of lake mixing processes, in order to examine the effects of surface chemical exchange on vertical concentration distribution.

One-dimensional models of lake mixing are typically employed for water bodies which experience greater horizontal mixing than vertical, such as Lake Ontario. Variations in density and concentration are much more pronounced vertically, so horizontal properties are assumed to be constant [10]. Vertical diffusion results from turbulent energy inputs at the surface, such as heating, cooling and wind [12]. Consequently, the surface waters become quite well mixed, while the deeper waters may be relatively quiescent. This upper region of the lake is known as the mixed layer or epilimnion; it is generally assumed that the water density is constant throughout this mixed layer. The deeper, unmixed waters are referred to as the hypolimnion.

Mixed layer modelling involves a number of complex processes, and although it has been studied since 1955, it is still incompletely understood [14]. Complicated turbulent transport phenomena must be quantified to provide accurate parameterization of the vertical mixing mechanisms in the epilimnion [18]. Little is known about the colder waters at the bottom of stratified lakes, but vertical transport in this region is typically modelled as diffusive [1, 12]. Lake mixing models must evaluate the amount of turbulent kinetic energy available for mixing, and determine whether any of the hypolimnetic waters
will become entrained by the mixed layer.

Most one-dimensional models of lake dynamics predict vertical temperature distributions. Water temperature is the simplest quantity to measure in order to validate the model’s accuracy; chemical concentrations are typically harder to obtain. Mackay [28, 32] points out that the degree of accuracy in these types of models is difficult to ascertain. Environmental concentrations are continually fluctuating in time and space, and data are scarce and unreliable. Additionally, there are many parameters which must be specified for a given system, and these are subject to large uncertainties. Often, a verification of a model’s robustness can only be made against a few data points, and calibrations of the models are based on trial and error.

Imberger and his research team are recognized as leaders in the field of lake modelling [14]. The Centre for Water Research at the University of Western Australia first developed the Dynamic Reservoir Simulation Model (DYRESM) in 1979, to predict long-term vertical temperature structures in a lake [21]. It has been implemented internationally on over one hundred lakes since that time, including the Great Lakes. DYRESM was modified in this project to simulate chemical concentrations, specifically Lindane, in Lake Ontario, resulting from air-water gas transfer.

The water quality of the Great Lakes is of concern because they are subject to large-scale anthropogenic emissions due to the high population density on their shores. Although production of certain toxic chemicals has decreased over the last decade [27], persistent compounds remain in the region and still affect water concentrations.

The development of the Lindane model is described in chapter 2. Descriptions of the mixing processes and air-water gas exchange algorithms are provided. DYRESM has options for including inflowing and outflowing rivers, and there are detailed algorithms for heating and cooling, surface layer mixing, and deep water diffusion. For this model, surface chemical flux was added to DYRESM, and the code was modified to predict concentrations. Meteorological and bathymetric data for this study were obtained from the Canadian Centre for Inland Waters, who performed extensive field measurements on Lake Ontario during the International Field Year on the Great Lakes 1972/1973. Lindane concentrations were obtained from several different sources [25, 27, 35, 43, 44].

The results of the Lindane simulations are presented and discussed in chapter 3. A baseline model was run using reasonably well-established Lindane concentrations in the lake and the atmosphere. The predictions of several theoretical scenarios were compared to the results from this baseline simulation. The case studies investigated include a doubling in atmospheric concentration of Lindane, a global climate change scenario, and two cases of a short-term elevation in air concentration, to mimic agricultural crop
spraying.

The appendices include: an analytical solution which was used to evaluate the diffusion subroutines (appendix A), properties of Lindane (appendix B), a conversion chart from Julian days to standard dates (appendix C), results of tests which were run to determine the model's physical stability limits (appendix D), and the FORTRAN code for the new model including relevant data files on diskette (appendix E).
Chapter 2

Model Development

The Dynamic Reservoir Simulation Model (DYRESM) is a one-dimensional vertical model of the dynamics of lakes and reservoirs of medium to large size. The original FORTRAN program, first developed in 1977, provides daily predictions of the vertical distribution of temperature and salinity within a lake. The modified version presented in this thesis, DYRESM-Ont, predicts lakewide concentrations of pollutants from inflowing rivers and atmospheric sources.

DYRESM has been used successfully on more than one hundred different lakes and reservoirs internationally, including Lake Ontario [5]. Subroutines for water quality and winter ice conditions have been incorporated in previous versions. In this research, algorithms for air-water gas exchange were added, and several scenarios were investigated.

2.1 Assumptions and Limitations

In a vertical one-dimensional model, properties are assumed to be a function of depth only. To accomplish this with DYRESM, the lake is divided into a series of slab-like layers (≤ 150 layers) with constant density and concentration in each.

Numerical models of this type have been used since the 1960’s for long-term temperature predictions because they provide reasonably accurate results while minimizing the number of computations, and thus, the total running time [10]. However, mixing processes in lakes are not well understood, and over-simplifications can lead to errors. In DYRESM, Imberger and Patterson [5, 21, 40] have parameterized the physical mixing processes rather than evaluating different mechanisms independently, to improve the accuracy of the predictions. Density stratification inhibits excessive vertical motions, and horizontal convection is assumed to balance lateral density differences quite rapidly [5].
To use a 1-D model, several conditions must be met to ensure that there is little horizontal variation. Imberger and Patterson [21] define several non-dimensional numbers for this purpose.

To determine the departure from one-dimensionality, the Wedderburn number $W'$ measures the activity within the mixed upper layer due to surface winds:

$$ W = \frac{g' h}{u_* L} $$  \hspace{1cm} (2.1)

where $g' = \frac{g \Delta \rho}{\rho_o}$ \hspace{1cm} (2.2)

where $g'$ is the effective reduced gravity over the thermocline computed from the reference density of the upper layer $\rho_o$ and the lower layer density $\rho_o + \Delta \rho$. $h$ is the depth of the mixed layer, $u_* = \sqrt{\tau/\rho}$ is the friction velocity at the surface, and $L$ is the basin scale. For one-dimensionality, $W \geq O(1)$. Lake Ontario meets this constraint with $W' \approx 2$.

The Coriolis effect of the earth’s rotation will cause internal waves in the lake unless the following condition is met:

$$ \frac{g' \delta}{f^2 B^2} < 1 $$  \hspace{1cm} (2.3)

where $g'$ is the reduced gravity over the velocity depth scale $\delta$, $f$ is the Coriolis parameter, and $B$ is the width of the lake. For Lake Ontario, $\frac{g' \delta}{f^2 B^2} \approx 0.02$, and it is therefore not subject to strong internal waves resulting from the Coriolis effect.

The internal Froude number $F_i$ determines the extent of vertical movement from inflowing rivers. For a 1-D constraint,

$$ F_i = \frac{U}{\sqrt{g' H}} < 1 $$  \hspace{1cm} (2.4)

where $U$ is the inflow velocity, $g'$ is the reduced gravity between the river and the lake, and $H$ is the lake depth. In Lake Ontario, $F_i \approx 0.5$.

Similarly, the outflow will not cause problems if its Froude number $F_o$ satisfies the following:

$$ F_o = \frac{Q}{g'^{3/2} H^{5/2}} < 1 $$  \hspace{1cm} (2.5)

where $Q$ is the rate of discharge. For more information about these non-dimensional numbers, refer to Imberger and Patterson [21], or the users’ guides [5, 40]. The outflow Froude number in Lake Ontario is typically just below this maximum, with $F_o \approx 0.9$.

Lake Ontario is long and narrow, but it is also deep ($\approx 239 m$). The lake experiences much more rapid mixing in the transverse and longitudinal directions than vertically by-
many orders of magnitude [10], which makes it a suitable candidate for vertical modelling. Since horizontal properties can be considered constant. Boyce et al. [4] determined that Lake Ontario meets the criteria for one-dimensionality, and confirmed their simulated temperature predictions by comparison to measured data.

To include concentration in DYRESM, the chemicals investigated are assumed to be conservative, non-biologically reactive tracers that do not affect water density. For highly soluble gases such as Lindane, surface gas exchange is considered to be a more significant chemical pathway than wet or dry deposition [42, 44]. Finally, mass is assumed to diffuse through the hypolimnion by the same mechanisms as heat diffusion [10].

2.2 Model Description: Mixing in Lakes

In colder climates such as Canada, a typical reservoir or lake possesses a well-defined thermal structure, with periods of temperature stratification for part of the year. A warmer surface layer floats above the colder, deeper waters in the summer. When the upper layer cools in the winter, there is an overturning or thermal inversion, which creates nearly isothermal conditions over the depth [34]. Lake Ontario is stratified from early summer through late autumn, and experiences vertical mixing during the winter months.

Generally, stratification in lakes is characterized by three regions: the epilimnion or mixed surface layer, which is subjected to the greatest disturbances; the colder and deeper hypolimnion, which is very inactive as it receives little energy for mixing; and the thermocline, a thin slice of steep temperature gradients which separates the two regions and cushions the hypolimnion from external forces.

The phenomenon of stratification is incorporated into DYRESM, by separating the lake into a set of slab-like layers, which are each assumed to be individually homogeneous in all properties. Layer thicknesses may vary with depth. Physical processes such as mixing, buoyancy changes (due to salinity or temperature variations), inflow and outflow are simulated by combining layers or changing a layer’s volume.

Heat transfer across the air-water interface is computed from measured surface air temperature, wind speed, cloud cover, humidity, and incident short-wave radiation. Temperatures and salinities are specified daily for major inflowing or outflowing rivers, such as Lake Ontario’s major inflow, the Niagara River, and its major outflow, the St. Lawrence River. Heat is then transported vertically through the water column, which includes the epilimnion, the hypolimnion, and the thermocline, the location of which is determined from calculated temperature gradients. The surface layers are subject to mixing from wind, breaking waves, shear due to currents, and convective cooling; salinity and temper-
nature are equally distributed throughout this well-mixed region. Below the thermocline, mixing is influenced by only a fraction of the turbulent energy available at the surface. Diffusion, changes in lake stratification, and a very small percentage of stirring by the wind contribute to the distribution of tracers, such as heat and salt, in the deep waters.

Five computational algorithms describe the primary processes in DYRESM:

- HEATR, for heating throughout the water column and cooling at the surface;
- MIXER, for surface mixed layer dynamics;
- DIFUSE and FCT, for hypolimnetic diffusion;
- INFLOW, for effects of inflowing rivers; and
- OUTFLO, for waters withdrawn from the reservoir.

Data is provided on a daily basis, a timescale which is sufficient for large-scale or slower processes, such as inflow or outflow. However, in order to accurately simulate continuous mixing in a lake, a sub-daily time step of 15 minutes is applied to the heating and mixing algorithms. Consequently, HEATR, MIXER, DIFUSE and FCT are called sequentially every quarter hour, while INFLOW and OUTFLO are only accessed once per day. The new subroutine GASTRANS, described in section 2.3., was added to the sub-daily loop immediately after HEATR. The chemical input to the surface is computed every 15 minutes to approximate continuous gas exchange as closely as possible. However, gas transfer rates, obtained from GASTRANS, are calculated every six hours, from wind speeds which are provided only four times per day.

Several additional service functions and subroutines are employed to determine density, layer thickness and overall stability of the lake. These are not shown in figure 2.1, which is a flowchart of the fundamental processes operating in DYRESM-Out. An overview of the theory behind the primary algorithms is included in this chapter; for more detailed information, refer to McCrann [36], Fischer et al. [10], Imberger and Patterson [21], or the DYRESM user guides [5, 40].

### 2.2.1 Surface Heat and Mass Transfer

Every 15 minutes, HEATR computes the meteorological forcing, which consists of evaporative and conductive heat flux, as well as long- and short-wave radiative absorption. Evaporation, conduction and long-wave radiation affect the surface layer only, while short-wave radiation penetrates to deeper waters. The resultant heat transfer from the
Figure 2.1: Flowchart of DYRESM-Ont.
uppermost to the lower layers is calculated by DYRESM after the inputs have been determined.

Air temperature, wind speed and vapour pressure (humidity) at the surface of the lake are only provided on a daily basis. In order to perform computations every 15 minutes, additional equations are necessary. Bulk aerodynamic formulae for turbulent transfers of moisture ($E$) and heat ($\tilde{H}$), represent evaporative and conductive heat fluxes into the top layer [21], and are called by DYRESM once per time step.

$$E = -C_W U (q - q_s) \rho$$  \hspace{1cm} (2.6)

$$\tilde{H} = -C_H U (T - T_s) \rho C_p$$ \hspace{1cm} (2.7)

where $C_W$ and $C_H$ are the bulk transfer coefficients for moisture and heat. $C_p$ is the specific heat of water, $\rho$ is the density of air, $U$ is the wind speed, $q$ is the humidity, and $T$ is the air temperature. Quantities measured at the surface are subscripted with $s$.

During daylight hours, transfers due to radiative heating result from both long- and short-wave radiation. Long-wave radiation is absorbed ($Q_{AC}$) and emitted ($Q_{W}$) by only the uppermost layer [21].

$$Q_{AC} = 0.97 \frac{\text{sunratio}}{\epsilon}$$

$$Q_{W} = \epsilon \sigma T^4$$  \hspace{1cm} (2.8)

where $\epsilon$ is the emissivity of the water surface ($= 0.96$), $\sigma$ is the Stephan-Boltzman constant ($= 2.0411 \times 10^{-7} \text{kJ/m}^2 \text{hr}^{-1} \text{oK}^{-4}$), sunratio represents the ratio of sunshine hours to daylight hours, and $T$ is the absolute surface temperature.

Short-wave radiation penetrates below the surface layer, heating the water column. This absorption, $Q(z)$, is modelled by Beer's law [21].

$$Q(z) = Q_s (\beta_1 e^{-\eta_1 z} + \beta_2 e^{-\eta_2 z} + \beta_3 e^{-\eta_3 z})$$ \hspace{1cm} (2.10)

where $Q_s$ is the radiation intensity at the surface, $z$ is the depth, $\eta_1$, $\eta_2$ and $\eta_3$ are attenuation coefficients, and $\beta_1$, $\beta_2$ and $\beta_3$ are intensity fractions, such that $\beta_1 + \beta_2 + \beta_3 = 1.0$.

Once the external inputs have been computed, the total heat absorbed by each layer is evaluated by DYRESM as:

$$\Delta Q_n = A_{n-1} (Q_n - Q_{n-1}) + (A_n - A_{n-1}) Q_n$$ \hspace{1cm} (2.11)

where $Q_n$ is the sum total of the radiation intensity arriving at the top of layer $n$, and $A_n$
is the area of the top surface of layer \( n \). For the uppermost layer, \( Q_n = E + \dot{H} + Q_{AC} + Q_W + Q_s \). Below the surface, only the effects of short-wave radiation and absorption of heat from neighbouring layers will alter a layer's temperature.

Before returning to the main program, HEATR adjusts layer heights and salinities to account for the effects of rainfall and evaporation.

In HEATR, the minimum time step is 15 minutes, and the maximum is six hours. For efficiency, the subroutine will attempt to perform all the calculations for a six hour time step, with the following limits: there is a maximum change of 3°C in surface temperature allowed during the total time period; and a maximum increase in kinetic energy equivalent to 10 cm s\(^{-1}\) in mixed layer mean velocity (refer to Imberger and Patterson [21] for further details). If either of these limits is exceeded, the time step is decreased an appropriate amount. At the minimum interval of 15 minutes, there is no realistic possibility of reaching either limit. The time step was therefore fixed at 15 minutes in the modified version, DYRESM-Ont.

### 2.2.2 Mixed Layer Dynamics

In a stratified lake, the epilimnion is formed as a result of mixing due to surface cooling and winds. The depth of the mixed layer in Lake Ontario typically varies from several metres in the summer down to the lakebed in the winter, when the lake becomes fully mixed. In DYRESM, layers of equal densities are identified and amalgamated into a single mixed layer with constant properties throughout.

DYRESM models the energetics of epilimnetic mixing in subroutine MIXER (and affiliated subroutine KH). A turbulent kinetic energy model is employed by MIXER to determine the deepening of the mixed layer from the energy available to the hypolimnion. Four primary processes are examined:

- **Convective overturn**, where surface cooling creates density instabilities in the upper layer structure;

- **Stirring**, due to winds at the surface which contribute to the mixing of the epilimnion. A small percentage of this energy reaches the hypolimnetic interface;

- **Shear production**, whereby the horizontal motion of the mixed layer may contribute some kinetic energy to the upper layers of the hypolimnion; and

- **Billowing**, caused by Kelvin-Helmholtz shear instabilities at the interface between the hypolimnion and the epilimnion, which smear out the sharpest density gradients between adjacent layers near the thermocline.
In MIXER, algorithms for each of these processes determine the energy made available for deepening the mixed layer. If the available energy equals or exceeds the required energy limit, deeper layers will be entrained by the epilimnion. Otherwise, the energy is stored for use in the next time step [5].

After MIXER, DYRESM returns to the main program with a stable density profile, a new mixed layer depth, and modified temperatures, salinities and concentrations throughout the lake.

**Convective Overturn**

MIXER begins each cycle by determining if there is thermal instability, that is, if the uppermost layers are cooler and heavier than those below. If so, the top layers are mixed together. The centre of mass of the newly mixed layer, \( C_{mm} \), is then compared to the centre of mass of these same layers when unmixed, \( C_m \). If \( C_{mm} > C_m \), the structure is unstable, and deeper layers are mixed into the epilimnion until stability is achieved.

\[
C_m = \sum_{j=1}^{H} \frac{\rho_j}{\rho_m} \frac{1}{2} (d_j - d_{j-1})(d_j + d_{j-1}) \frac{1}{\sum_{j=1}^{H} \rho_j (d_j - d_{j-1})}
\]

\[
C_{mm} = \frac{d_H + d_{k-1}}{2}
\]

where \( \rho_j \) and \( d_j \) are the density and height of the \( j^{th} \) layer, and \( d_{k-1} \) and \( d_H \) represent the height of the base of the mixed layer and the height of the surface of the lake.

Potential energy is released as a buoyancy flux when the centre of mass is lowered to the new, stable configuration. This can be characterized by a turbulent velocity scale \( w_* \) [21].

\[
w_*^3 = \frac{g}{\rho_m \Delta t} \Delta h_{cm} \sum_{j=1}^{H} \rho_j (d_j - d_{j-1})
\]

where \( \Delta h_{cm} = C_m - C_{mm} \), \( \Delta t \) is the time step, and the mixed layer thickness is \( d_H - d_{k-1} \).

The energy from convective cooling available for mixing, \( E_{ac} \), may be written as:

\[
E_{ac} = \frac{C_k w_*^3 \Delta t}{2}
\]

where \( C_k \) is an input variable measuring stirring efficiency. This energy is incorporated into the stirring energy equation for further use in DYRESM.
Stirring

Surface winds stir the mixed layer, and a fraction of this kinetic energy penetrates below the thermocline. A turbulence scale \( q \) is introduced, which incorporates the effects of convective cooling and stirring.

\[
q^3 = w_*^3 + \eta^3 u_*^3
\]  
(2.16)

where \( \eta \) is a convective and stirring efficiency parameter, and \( u_* \) is the friction velocity.

This scale allows computation of the combined energy available due to stirring and convective overturn, \( E_{as} \), which is added to residual energy left over from the previous time step.

\[
E_{as} = \frac{C_k q^3 \Delta t}{2} + E_{as}
\]  
(2.17)

The energy required to entrain layer \( k - 1 \) into the mixed surface layer is \( E_r \):

\[
E_r = \left( \frac{\Delta \rho}{\rho} g h + C_t q^2 \right) \frac{\Delta h}{2}
\]  
(2.18)

where \( \Delta h \) is the thickness of layer \( k - 1 \), \( \Delta \rho/\rho = 2(\rho_{k-1} - \rho_m)/(\rho_{k-1} + \rho_m) \). \( h \) is the current depth of the mixed layer, and \( C_t \) is an input constant associated with unsteady effects.

This stirring process is repeated and deeper layers are entrained until \( E_{as} < E_r \) whereupon the energy from shear production is evaluated.

Shear Production

Strong winds at the surface of the lake may set up horizontal internal wave motions with a mean velocity shear \( \Delta U \):

\[
t \leq t_{eff} : \quad \Delta U = \frac{u_*^2 t}{h} + \Delta U_o
\]  
(2.19)

\[
t > t_{eff} : \quad \Delta U = 0
\]  
(2.20)

where \( \Delta U_o \) is the previous time step’s value of \( \Delta U \), and \( t_{eff} \) represents an effective cut-off time for the wave motion:

\[
t_{eff} = \frac{T_i}{4} \left( 0.587 \left\{ 1 - \text{sech} \left( \frac{T_d}{T_i} - 1 \right) \right\} + 1 \right)
\]  
(2.21)

where \( T_i \) is the wave period and \( T_d \) is the damping period for a lake of two primary layers.
as detailed in Imberger and Patterson [21].

The interface between the epilimnion and the hypolimnion experiences billowing, which smears out the sharply defined boundary by reducing density gradients between layers. The thickness of a billow, \( \delta \), will change by \( \Delta \delta \) during two consecutive time steps.

\[
\Delta \delta = \frac{0.6 U_{av} \Delta U_{av}}{g \delta \rho} \tag{2.22}
\]

with \( U_{av} = \frac{1}{\Delta t} \int_0^t \Delta U \, dt \) \tag{2.23}

where \( U_{av} \) will be calculated over the time step \( \Delta t \), or until \( t_{eff} \) is reached (if \( t_{eff} < \Delta t \)).

The energy available from shear production \( E_{ap} \) may now be evaluated [21].

\[
E_{ap} = C_s \left( U_{av}^2 \Delta h + \frac{U_{av} \Delta \delta}{6} + \frac{U_{av} \delta \Delta U_{av}}{3} \right) + \left( g \frac{\Delta \rho \delta \Delta \delta}{24 \Delta h} - g \frac{\Delta \rho \delta \Delta \delta}{12} \right) \tag{2.24}
\]

where \( \Delta h \) represents the change in mixed layer depth between time steps, and \( C_s \) is a shear production efficiency coefficient.

As in equation 2.18, the energy required to mix the layer below the current interface is:

\[
E_r = \left( \frac{\Delta \rho}{\rho} g h + C_l q^2 \right) \frac{\Delta h}{2} \tag{2.25}
\]

The shear production algorithm will continue to loop, deepening the mixed layer, until \( E_{ap} < E_r \). Then the Kelvin-Helmholtz billows are modelled by subroutine KH.

**Billowing**

Subroutine KH is an auxiliary operation to MIXER’s algorithms. If the thickness of the billows identified in the shear production computation is less than \( \delta_{min} \), then the interface between the hypolimnion and epilimnion will become unstable, and Kelvin-Helmholtz billows will be formed [21].

\[
\delta_{min} = \frac{0.3(\Delta U)^2}{g'} \tag{2.26}
\]

where \( g' \) is the effective reduced gravity over the depth.

In DYRESM, these billows are generated by splitting the affected shear zone into a number of layers with equal densities, and then smearing or blending them by mixing from the interface outwards, until a stable, less sharp gradient is achieved.

Following subroutine KH, DYRESM returns to MIXER, where new temperatures and concentrations are computed before exiting to the main program.
2.2.3 Diffusion in the Hypolimnion

Below the thermocline, there is little vertical mixing. The hypolimnion does not experience the full extent of the disturbances absorbed by the mixed surface layer, and is stabilized by a weak density gradient. According to Fischer et al. [10], there can be sporadic occurrences of vigorous hypolimnetic mixing events, which occur rapidly and occupy relatively small volumes. In DYRESM’s FCT and DIFUSE subroutines, the overall effect of these mixing processes is modelled as vertical diffusion over each time step. The following 1-D diffusion equation is employed to compute the diffusion below the thermocline:

\[
\frac{\partial Y}{\partial t} = \varepsilon_z \frac{\partial^2 Y}{\partial z^2}
\]  

(2.27)

where \( Y \) represents the conservative tracer in terms of temperature or concentration. \( t \) is the time, \( z \) is the depth, and \( \varepsilon_z \) is the eddy diffusivity \((m^2 s^{-1})\) [5].

Subroutine FCT evaluates the right-hand side of equation 2.27, and then subroutine DIFUSE uses a method of slopes to solve the left-hand side. In the current version of DYRESM, \( \varepsilon_z \) is taken as a sum of the molecular diffusivity, \( \varepsilon_{mol} \), and the Harleman diffusivity, \( \varepsilon_{hart} \). The latter was implemented by Dr. Paul Hamblin of CCIW [pers.comm.], and is a function of the lake’s potential energy combined with the relatively small effects of wind stirring at the surface and inflowing rivers.

\[
\varepsilon_{hart} = \frac{\alpha_1 (E_{wind} + E_{inflow}) z^2}{P_s}
\]  

(2.28)

where \( E_{wind} \) and \( E_{inflow} \) represent the power inputs due to wind stirring at the surface and the effect of inflowing rivers, \( z \) is the depth from the surface, \( P_s \) is the potential energy of the stratified lake or reservoir, and \( \alpha_1 \) is the percentage of the power which affects the hypolimnion (=0.02) [1].

These power inputs are defined as:

\[
E_{wind} = C u_*^3 A_s
\]  

(2.29)

where \( C \) is a parameter which incorporates the drag coefficient and sheltering from the wind [21], \( u_* \) is the friction velocity, and \( A_s \) is the surface area of the uppermost layer:

and

\[
E_{inflow} = \frac{g}{A_t} \int_0^h Q \rho \, dz
\]  

(2.30)

where \( Q \) is the river discharge into the lake, \( \rho \) is the density of the water, with the power computed over depth \( z \) and time \( \Delta t \).
The potential energy locked in stratification, $P_s$, is determined from the vertical distance between the centres of mass in the stratified and fully-mixed lake ($\Delta h_{cm}$):

$$P_s = g\Delta h_{cm} \int_0^H \rho A \, dz$$  \hspace{1cm} (2.31)

Finally, $P_s$, $E_{inflow}$ and $E_{wind}$ can be used to compute the mixing time scale, $T_m$:

$$T_m = \frac{P_s}{E_{wind} + E_{inflow}}$$  \hspace{1cm} (2.32)

In DYRESM, subroutines FCT and DIFUSE are called separately for the hypolimnetic mixing of heat and salt, and in the new model DYRESM-Ont. for Lindane.

### 2.2.4 Inflow

Inflow dynamics in a lake can be characterized by three possible stages, displayed in figure 2.2: inflow, surface intrusion and subsurface intrusion. First, the inflowing river enters the lake and pushes through the stagnant waters. If the river density is less than or identical to the reservoir's density, the water will flow over and into the surface waters. Otherwise, the heavier inflowing water will plunge down the side of the lake basin, entraining lake water, until the location at which buoyancy forces become equal: at this depth, the flow will intrude horizontally into the reservoir [21].

In DYRESM, subroutine INFLOW calculates the location of intrusion into the lake, the thickness and volume of the inserted inflowing water, and the new temperatures.
salinities and concentrations. INFLOW is called once per day, for up to four inflowing rivers, although only the Niagara River is incorporated into the Lake Ontario model.

Several parameters are necessary to incorporate the complicated inflow processes into DYRESM. The slope of the river bed $\phi$, the half angle of the river bottom $\alpha$ (assuming a triangular cross-section [10]), the drag coefficient $C_d$, and the daily inflow volume $Q$ are required inputs. From these, the internal Froude number $F_i$ is determined:

$$F_i^2 = \frac{\sin \alpha \tan \phi}{C_d} \left(1 - 0.85\sqrt{C_d \sin \alpha}\right)$$ (2.33)

As the inflow moves down the lake basin wall, it will entrain water from the lake, which will moderate the density differences. The entrainment coefficient, $E$, is:

$$E = \frac{\eta^3 C_k C_d^{3/2} F_i^2}{2}$$ (2.34)

where $\eta^3 C_k$ represents an efficiency (= 3.2) [10, 21].

For an inflowing river of triangular cross-section, there will be an initial inflow depth $h_o$.

$$h_o = \left\{\frac{2Q^2}{F_i g \Delta \rho \tan^2 \alpha}\right\}^{1/5}$$ (2.35)

where $\Delta \rho$ is the non-dimensional density difference between the inflow and the reservoir water, $(\rho_{in} - \rho_r)/\rho_r$.

Now the flowing depth at any time, $h$, can be evaluated [40].

$$h = \frac{4}{5} E \left(\frac{d_i - d_{i-1}}{\sin \alpha}\right) + h_o$$ (2.36)

where $d_i - d_{i-1}$ represents the thickness of layer $i$, since $d_i$ is the height of layer $i$ above the lakebed.

The inflowing volume $Q$ will entrain water from the reservoir at a rate $\Delta Q$, which can now be computed as:

$$\Delta Q = Q \left(\left\{\frac{h}{h_o}\right\}^{5/3} - 1\right)$$ (2.37)

The Grashof number, $Gr$, must be determined for further computations.

$$Gr = \frac{N^2 L^4}{\epsilon z^2}$$ (2.38)

where $N$ represents the Brunt-Vaisala frequency [40], $L$ is the reservoir length at the
point of insertion, and \( \epsilon_z \) is the vertical diffusivity.

The length of inflow intrusion into the reservoir at any depth, \( e \), is characterized by the non-dimensional number \( R = F_t Gr^{1/3} \).

\[
R < 1 \quad e = 0.574LR^{2/3} \left( \frac{tN}{Gr^{1/6}} \right)^{5/6} \\
R \geq 1 \quad e = 0.44LGr^{1/2} \frac{tN}{Gr^{1/6}}
\]  

(2.39)  
(2.40)

where \( t \) is the time over which the intrusion is computed (= one day in DYRESM).

Using the width at the intrusion entrance \( B \), the intrusion length \( e \), and the newly incremented inflow rate \( Q = Q + \Delta Q \), the thickness of insertion \( \delta \) can be computed.

\[
\delta = \frac{Q}{B} \left\{ 1 - \frac{e}{L} \right\}
\]  

(2.41)

Intrusion thickness \( \delta \) can be separated into upper and lower thicknesses \( \delta_t \) and \( \delta_b \) around the line of insertion, such that the following horizontal velocity profile is obtained in the layers immediately above and below the intrusion location:

\[
z \leq d_Z \quad u = \frac{u_{max}}{2} \left( \cos \left( \frac{\pi z}{\delta_b} \right) + 1 \right)
\]

(2.42)

\[
z > d_Z \quad u = \frac{u_{max}}{2} \left( \cos \left( \frac{\pi z}{\delta_t} \right) + 1 \right)
\]

(2.43)

and \[
\frac{u_{max}}{2} = \frac{Q}{\delta_t + \delta_b}
\]

(2.44)

where \( z \) is the vertical distance measured from the level of insertion \( d_Z \), and \( u_{max} \) is the inflow velocity at \( d_Z \).

From the thicknesses, the volume \( dV_i \) added to the layer above the level of insertion \( (d_Z) \) can be determined,

\[
dV_i = \frac{q}{\delta_t + \delta_b} \left( \frac{\delta_t}{\pi} \left\{ \sin \frac{\pi}{\delta_t} (d_i - d_Z) - \sin \frac{\pi}{\delta_t} (d_{i-1} - d_Z) \right\} + d_i - d_{i-1} + d_i - d_{i-1} \right)
\]

(2.45)

and a similar equation can be obtained for the volume added to the layer below.

After computation of the inflow volume and location, the temperatures, salinities and concentrations are recalculated for the affected sections of the lakes. DYRESM then adjusts layer thicknesses, renumbers the layers, and calls subroutine OUTFLO.

More detailed theory of inflow intrusion and mixing processes can be found in Fischer et al. [10] and Imberger and Patterson [21].
### 2.2.5 Outflow

The removal of discharge from a lake is modeled daily by subroutine OUTFLO, which is essentially the converse of INFLOW. The algorithms are simplified in DYRESM-Ont because the extrusion of water occurs at a single fixed outlet at the surface of Lake Ontario (the St. Lawrence River) [36], however, DYRESM is configured to permit up to three offtakes.

The thickness of the extrusion, \( \delta \), is calculated from the Froude number \( F_i \), the Grashof number \( Gr \), and the non-dimensional number \( R = F_i Gr^{1/3} \).

\[
R < 1 \quad \delta = 2 LF_i^{1/2} \tag{2.46}
\]
\[
R \geq 1 \quad \delta = \frac{2L}{Gr^{1/3}} \tag{2.47}
\]

with \( F_i = \frac{Q}{\Delta t B N L^2} \) \( (2.48) \)

and \( Gr = \frac{N^2 L^4}{\epsilon^2} \) \( (2.49) \)

where \( Q \) is the outflow volume, and \( \Delta t \), \( B \), \( N \), \( L \) and \( \epsilon \) are the time elapsed, width of extrusion, Brunt-Vaisala frequency [40], reservoir length at the surface, and vertical diffusivity, as discussed in the previous section [40, 21].

A simplification to equation 2.45 arises because the outflow is withdrawn from a single layer, and need not be apportioned into \( \delta_i \) and \( \delta_b \). Since there is no layer above the surface, \( \delta \) represents the total withdrawal thickness. The overall removal volume from the surface can therefore be described by:

\[
dV_H = \frac{Q}{\delta} \left( \frac{\delta}{\pi} \left\{ \frac{\pi}{\delta} (d_H - d_{H-1}) \right\} + d_H - d_{H-1} \right) \tag{2.50}
\]

where subscript \( H \) represents the surface, and \( d_H - d_{H-1} \) is the thickness of the top layer. If the outflow volume is greater than the surface layer volume, DYRESM amalgamates layers to accommodate the withdrawal.

Once the outflow volume is removed, layers are combined to account for the removal, and temperatures, salinities and concentrations are computed for both the lake and the outflowing river. Upon returning to the main program, DYRESM recalculates layer thicknesses and provides output before returning to the beginning of the daily loop.

### 2.2.6 Service Subroutines

Several subroutines are employed by DYRESM for general maintenance purposes:
• THICK maintains the layer volumes between specified limits;
• RESINT interpolates depths, volumes and areas from input data;
• DENSTY computes the density of water at a given temperature and salinity; and
• SATVAP calculates the saturated vapour pressure of air at a given temperature.

THICK

Subroutine THICK ensures that layer volumes are kept within the specified limits \( V_{\text{min}} \) and \( V_{\text{max}} \):

\[
V_{\text{min}} = \frac{V_{\text{lake}}}{N} \\
V_{\text{max}} = 4V_{\text{min}}
\]

(2.51) \hspace{1cm} (2.52)

where \( V_{\text{min}} \) and \( V_{\text{max}} \) are the minimum and maximum allowable layer volumes. \( V_{\text{lake}} \) is the capacity of the lake, and \( N \) is the maximum number of layers allowed by DYRESM (= 150).

A maximum layer volume is established to provide a reasonable degree of resolution. and the minimum volume prevents an excessive number of computations. For any volume \( V_i \), if \( V_i > V_{\text{max}} \), the layer is split into two layers with equal properties. Likewise, if \( V_i < V_{\text{min}} \), the layer is amalgamated with its smallest neighbour. All layers are then renumbered.

THICK is called after any subroutine which may have affected layer volumes, with the exception of MIXER, where an intentionally large mixed surface layer is created [21].

RESINT

Whenever there has been a change to the geometric properties of any layers, RESINT is called. Using interpolation, this subroutine computes layer volumes and surface areas from heights above the lakebed, or layer heights and surface areas from given volumes [40].

The relationships have the form:

\[
\frac{V_i}{V_{i-1}} = \left[ \frac{d_i}{d_{i-1}} \right]^{a_i} \\
\frac{A_i}{A_{i-1}} = \left[ \frac{d_i}{d_{i-1}} \right]^{b_i}
\]

(2.53) \hspace{1cm} (2.54)
where $V_i$, $d_i$ and $A_i$ represent the cumulative volume, height from lakebed and surface area of the $i^{th}$ layer [21], and exponents $a_1$ and $b_1$ are computed in DYRESM from the initial bathymetric data. Finally, individual layer volumes are calculated.

**DENSTY**

Any alterations in the temperature or salinity of a layer requires recomputation of the water density. DENSTY provides a numerical value, given temperature and salinity, based on a formula by Chen and Millero, 1977 [21].

**SATVAP**

Daily saturated vapour pressure data for the surface of a lake is generally not available. SATVAP evaluates the daily saturated vapour pressure, given air temperature at the surface.

### 2.3 DYRESM-Ont: Modelling Concentration

DYRESM-Ont was created by adding algorithms for air-water gas exchange to the original version of DYRESM. Subroutine GASTRANS was added into the sub-daily loop between HEATR and MIXER, so that it could be accessed every time step (see figure 2.1). The concentration in Lake Ontario of the organochlorine pesticide, Lindane, was the subject of this study, but DYRESM-Ont can be used on different lakes to investigate other chemicals, provided they do not exceed the stability limit described in section 2.4.

In DYRESM-Ont, mass may enter the lake by flux through the water surface, or in the inflowing Niagara River. Once in Lake Ontario, the chemical is subject to mixing in the epilimnion and the hypolimnion. Mass is removed from the lake by the outflowing St. Lawrence, or as gaseous flux into the air. The chemical pathways modelled by DYRESM-Ont are illustrated in figure 2.3.

Inflow and outflow subroutines add or remove chemical mass once per day, and surface flux and lake-wide mixing occur on the 15 minute sub-daily time step. A flowchart for chemical transport is shown in figure 2.4.

Chemical transport mechanisms were modelled in the same way that DYRESM accounts for heat and salt. Similar to temperature and salinity, concentration is assumed constant throughout any single layer, and any processes affecting the geometry of a layer
Figure 2.3: Chemical pathways modelled by DYRESM-Ont.

will change the concentration. Continuous mass balance checks were made in all simulations to ensure that mass was conserved.

To incorporate concentration into DYRESM, input files were added, and additional code was included in subroutines MIXER, FCT, INFLOW, OUTFLO, and THICK. A new series of algorithms, based in subroutine GASTRANS, determines the rate of gas exchange between the air and the water, and injects mass into the surface of the lake.

**Input Data**

To add concentration information, two input files and a subroutine were created. The first data file allows the user to specify the chemical, its molecular diffusivity, its average concentration in the air, and the initial concentrations at various depths in the lake. The second file provides the daily concentration in the inflowing rivers. Subroutine LINDAIR was added to DYRESM-Ont to estimate the daily concentration of Lindane in the air above Lake Ontario, given air temperature (refer to section 2.5.4). If the air concentration is not specified daily, DYRESM-Ont will use the average value given in the first input file.

**MIXER**

In the mixed layer formed by DYRESM-Ont, all properties, including temperature, salinity, and concentration, are constant. As deeper waters are entrained by the epilimnion, the chemical present in those waters is distributed throughout the newly formed mixed layer.
Figure 2.4: Flowchart for chemical transport in DYRESM-Ont.
FCT

Diffusion of the chemical through the hypolimnion is modelled by FCT and DIFUSE with the same equations used for heat and salt. The chemical's molecular diffusivity $\epsilon_{mol}$ varies with temperature, and is computed for each layer. This is combined with the turbulent Harleman diffusivity, $\epsilon_{harl}$ to solve the diffusion equation for concentration.

$$\frac{\partial C}{\partial t} = \epsilon_z \frac{\partial^2 C}{\partial z^2}$$

(2.55)

where $C$ is the concentration, $\epsilon_z = \epsilon_{harl} + \epsilon_{mol}$, and $t$ and $z$ are the time and depth.

INFLOW

In DYRESM-Ont, the inflowing Niagara River injects mass into the lake on a daily basis. The concentration in the inflow must be included in an input file. When the inflow volume is entrained at various depths, the mass transported by that volume is dispersed through the layers by which the flow is absorbed.

OUTFLO

The daily St. Lawrence outflow has the same concentration as the uppermost layer, since it is modelled as withdrawal from the surface. If the top two layers must be amalgamated to allow for withdrawal, the concentration will be distributed over both equally and then removed in the outflowing river.

THICK

As layers are split or merged, the properties are distributed accordingly. When two layers are combined in subroutine THICK, the mass from each is added, then divided by the total volume to evaluate the new concentration.

GASTRANS

The subroutine GASTRANS, used to determine the flux across the surface of the lake, is based upon the work of Hancock [13]. GASTRANS computes the values of the gas transfer velocity $K_{tot}$, the solubility $\beta$ and the percent supersaturation $\Delta$, given the air temperature $T_a$, the temperature of the surface layer of water $T_s$, and the wind speed $u$. These variables can then be used to evaluate the rate of flux through the air-water interface.
GASTRANS is currently configured to evaluate gas transfer velocities for Lindane, carbon dioxide, and hexachlorobenzene. Other gases can be specified with some adjustments to the subroutine. Fundamental properties for the compound of interest are computed first, then used to determine the overall diffusive transfer velocity $K_{ol}$ and the total transfer velocity $K_{tot}$.

First, the viscosity of water $\mu_w$ (in centipoise, cP) is determined, based on equations from the CRC Handbook [6]. For temperatures between 0°C and 20°C,

$$\log_{10} \frac{\mu_w}{\mu_{20}} = \frac{1301}{998.333 + 8.1855(T_w - 20) + 0.00585(T_w - 20)^2} - 1.30233 \quad (2.56)$$

and for temperatures above 20°C but below 100°C,

$$\log_{10} \frac{\mu_w}{\mu_{20}} = \frac{1.3272(20 - T_w) - 0.001053(T_w - 20)^2}{T_w + 105} \quad (2.57)$$

where $T_w$ is the temperature of water in °C and $\mu_{20}$ represents the viscosity at 20°C. Below 0°C, $\mu_w$ increases approximately linearly, from 1.798 cP at 0°C to 2.55 cP at -10°C [6].

The viscosity of water is used to determine the diffusivity of Lindane in water, $D_w$, and the diffusivity in air, $D_a$ may also be evaluated:

$$D_w = \frac{13.26 \times 10^{-9}}{\mu_w^{1.14} V_L^{0.589}} \quad (2.58)$$

$$D_a = 10^{-7} \times \frac{T_a^{1.75} \sqrt{\left(\frac{1}{m_a} + \frac{1}{m_L}\right)}}{P(V_a^{1/3} + V_L^{1/3})^2} \quad (2.59)$$

with $D_w$ and $D_a$ in $m^2 s^{-1}$, and where $T_a$ is the absolute air temperature, $m_a$ is the molecular mass of air ($= 28.97 \text{ g mol}^{-1}$), $m_L$ is the molecular mass of Lindane ($= 291 \text{ g mol}^{-1}$), $P$ is the gas phase pressure ($= 1 \text{ atm}$ [15]), and $V_a$ is the molecular volume of air ($= 20.1 \text{ cm}^3 \text{ mol}^{-1}$). $V_L$ is the molar volume of Lindane, which is dependent on the arrangement of atoms within a molecule ($= 207.8 \text{ cm}^3 \text{ mol}^{-1}$), as calculated by Hancock [13].

Now, the dimensionless Schmidt numbers for air and water ($Sc_a$ and $Sc_w$) can be calculated. These represent the ratio of the molecular transport properties [23].

$$Sc_a = \frac{\mu_a/\rho_a}{D_a} \quad (2.60)$$
where $\rho_w$ and $\rho_a$ represent the densities of water and air.

Next, GASTRANS computes the dimensionless Bunsen solubility $\beta$, using the Henry’s law constant $H$, which is the ratio of a chemical’s concentration in the gas phase to that in the aqueous phase at equilibrium [45]. In other words, the concentration in the air and the water on opposite sides of an interface will differ at equilibrium, in a ratio which is dependent on the compound’s solubility. For example, a very soluble chemical will have a higher concentration in water than in air at equilibrium, and therefore a low Henry’s law constant.

\[
H = \frac{10^m \rho_w + b}{RT_w}
\]

(2.62)

\[
\beta = \frac{1}{H}
\]

(2.63)

where $R$ is the universal gas constant, $T_w$ is the absolute water temperature, and $m$ and $b$ are constants with $m = -2382$ and $b = 7.54$.

The speed at which a chemical passes through an air-water interface is different on each side of the air-water boundary due to its solubility [45]. The overall transfer velocity $K_{ol}$ is composed of a transfer velocity on the air-side of the interface $K_a$, and a transfer velocity on the water-side $K_w$, partitioned by the Henry’s law constant:

\[
\frac{1}{K_{ol}} = \frac{1}{K_w} + \frac{1}{K_a H}
\]

(2.64)

The air-side transfer velocity can be computed [46]:

\[
K_a = 1.0 \times 10^{-3} + 46.2 \times 10^{-3} u_* S_{cw}^{-0.67}
\]

(2.65)

and the water-side transfer velocity:

\[
K_w = 1.57 \times 10^{-4} u_* \sqrt{\frac{600}{S_{cw}}}
\]

(2.66)

where the friction velocity $u_*$ is dependent on the wind speed $u$ (both in m s$^{-1}$), and reflects the fact that gas transfer is smaller at lower wind speeds:

\[
\begin{align*}
    u < 11 \text{ m s}^{-1} & \quad u_* = u \sqrt{1.2 \times 10^{-3}} \\
    11 \leq u \leq 25 \text{ m s}^{-1} & \quad u_* = u \sqrt{(0.49 + 0.065u) \times 10^{-3}}
\end{align*}
\]

(2.67) (2.68)
For gases which are very soluble in water such as Lindane, \( \beta \) will be large, and \( H \) will be small. Thus, the transfer velocity through the water-side is high, such that equation 2.64 yields the following relationship:

\[
K_w \gg K_a H \Rightarrow K_{al} \approx K_a H 
\]  
(2.69)

This is known as being air-side limited. Similarly, for insoluble gases such as carbon dioxide or oxygen, the transfer through air is faster than through water because \( H \) is large, so the chemical is water-side limited:

\[
K_w \ll K_a H \Rightarrow K_{al} \approx K_w 
\]  
(2.70)

As the wind speed increases, bubbles can provide a parallel pathway for chemicals through the water surface, resulting in a total transfer velocity \( K_{tot} \).

\[
K_{tot} = K_{al} + K_b
\]  
(2.71)

where \( K_b \) is the bubble-mediated transfer velocity [50].

There is an intensive algorithm in DYRESM-Ont to determine \( K_b \), based on the work of Woolf [50, 51, 52]. The bubble-mediated transfer velocity is evaluated from input data which includes \( u, T_a, T_w \), bubble population characteristics and whether there are contaminants in the water\(^1\). However, for air-side limited gases, bubbles were found to have a negligible effect on the total transfer velocity [13]. For example, for Lindane at \( T = 20^\circ C \) and \( u = 12 m s^{-1} \), \( K_{al} = 0.35 cm h^{-1} \), \( K_b \approx 0 \) and the supersaturation term \( \Delta = 0 \). Therefore:

\[
K_{tot} = K_{al} = \left( \frac{1}{\frac{1}{K_w} + \frac{\beta}{K_a}} \right)
\]  
(2.72)

remembering that \( \beta = 1/H \).

The input data \( (T_a, T_w, \text{and } u) \) are provided on different time scales: \( T_a \) is a daily value, \( u \) is given every six hours, and \( T_a \) is computed over each 15 minute time step. To account for the constantly changing \( T_a \), GASTRANS may be called every 15 minutes. However, a trial run which called the subroutine with this frequency demonstrated negligible differences when compared to results generated by a run which evaluated \( K_{tot}, \beta \) and \( \Delta \) only once every six hours. Also, the significant increase in running time associated

\(^1\)The equations for determining \( K_b \) are not included in this thesis because they were not applicable to Lindane. However, they are present in the GASTRANS subroutine and are operational. For more details, please refer to Hancock [13] or Woolf [50, 51, 52].
with calling GASTRANS every 15 minutes influenced the decision to use a six hour time step with this subroutine in DYRESM-Ont. Thus, $K_{\text{tot}}$, $\beta$ and $\Delta$ are calculated for each six hour period.

To accurately model the continuous exchange of gases between the air and the lake, the flux through the surface of Lake Ontario is computed every 15 minutes with the values for $K_{\text{tot}}$, $\beta$ and $\Delta$ provided by GASTRANS. The equation for air-water flux is given by Hancock [13] as:

$$F = K_{\text{tot}}(\beta(1 + \Delta)C_a - C_w)$$  \hspace{1cm} (2.73)

where $F$ is the rate ($kg\ m^{-2}\ s^{-1}$), $K_{\text{tot}}$ is the total gas transfer velocity ($m\ s^{-1}$), $\beta$ is the dimensionless solubility, $\Delta$ is the percent supersaturation [52], $C_a$ is the air concentration, and $C_w$ represents the concentration in the uppermost layer of the lake. The supersaturation is negligible in air-side limited gases such as Lindane, while the solubility is high.

At the beginning of each time step, DYRESM-Ont computes the mass of chemical input or output for the following 15 minute period, and injects it into or removes it from the surface layer.

$$F_m = F(A_s\Delta t)$$  \hspace{1cm} (2.74)

where $F_m$ is the total mass input or output over the time step $\Delta t$, and $A_s$ is the surface area of the lake.

The change in surface concentration, $\Delta C$, during a time step $\Delta t$, is given by:

$$\Delta C = \frac{F_m}{V_s}$$  \hspace{1cm} (2.75)

where $V_s$ is the volume of the surface layer.

Equilibrium occurs when there is no flux, that is, at $C_w = \beta(1 + \Delta)C_a$. To avoid over-saturation, the surface layer cannot exceed this equilibrium concentration. A maximum increment of $\Delta C_{\text{max}} = \beta(1 + \Delta)C_a - C_w$ is specified in DYRESM-Ont, which limits the total mass of chemical that can be absorbed by the surface during a single time step.

In simulations of air-side limited gases such as Lindane, $\Delta \approx 0$, and the lake remains at a near-equilibrium state as the chemical is continually mixed over the depth, with $C_w \approx \beta C_a$. 
2.4 Model Stability

Certain thresholds to preserve numerical stability in DYRESM-Ont were proposed, based on the amount of flux into the lake over a single time step.

The equation for flux through the surface of the lake given in the previous section is:

\[ F = K_{tot}(\beta(1 + \Delta)C_a - C_w) \]  \hspace{1cm} (2.76)

From this, a mass injection \( F_m \) into the surface layer is computed for each time step. To avoid over-saturation, the change in surface layer concentration during a single time step is limited to \( \Delta C_{\text{max}} \):

\[ \Delta C_{\text{max}} = \beta(1 + \Delta)C_a - C_w \]  \hspace{1cm} (2.77)

DYRESM-Ont's 15 minute time step therefore imposes a limitation in the type of chemicals which can be modelled. The model will provide accurate predictions as long as \( \Delta C \ll \Delta C_{\text{max}} \); however, when \( \Delta C \sim \Delta C_{\text{max}} \), the model may be subject to numerical instabilities. In other words, when the predicted flux is too large, DYRESM-Ont attempts to inject an excessive mass into the uppermost layer.

A stability threshold is obtained from the above equations. Mixing only occurs every 15 minutes, so the chemical remains in the surface layer, unmixed, until the next time step. For the purposes of determining a stability limit, the actual surface concentration is considered to be closely approximated by the unmixed concentration immediately after the mass is injected. For stability:

\[ \frac{\Delta C}{\Delta C_{\text{max}}} \ll 1 \]  \hspace{1cm} (2.78)

\[ \frac{F_m}{V_s} \ll \frac{\beta(1 + \Delta)C_a - C_w}{V_s} \]  \hspace{1cm} (2.79)

\[ \frac{FA_s\Delta t}{V_s} \ll \frac{F}{K_{tot}V_s} \]  \hspace{1cm} (2.80)

\[ \therefore K_{tot} \ll \frac{V_s}{A_s\Delta t} \]  \hspace{1cm} (2.81)

where \( \frac{V_s}{A_s} \approx H_s \)

\[ \text{hence } \Delta t \ll \frac{H_s}{K_{tot}} \]  \hspace{1cm} (2.82)

where \( C_w \) is the water concentration prior to mass injection and \( H_s \) is the depth of the uppermost layer.

Hence, with DYRESM's current 15 minute time step, chemicals must have a relatively
small $K_{tot}$, which is true for most air-side limited, highly soluble gases. Minimum and maximum layer volumes are presently dictated by DYRESM's THICK subroutine (see section 2.2.6), but if there were no volume restrictions, a very thin surface layer could create stability problems by becoming over-saturated very quickly.

For the scenarios presented in this thesis, predictions of Lindane concentrations were stable. However, test runs that used chemicals whose $K_{tot}$ exceeded the limit given in equation 2.80, at any point during the simulation, resulted in inaccurate predictions due to numerical instability. An investigation of the model's physical solubility limits, based on simulations using DYRESM, is presented in appendix D.

To facilitate the study of water-side limited gases, future work with this model could include a decrease of the minimum time step.

2.5 Data for DYRESM-Ont

To create a baseline model with DYRESM-Ont for comparison to test scenarios, data for Lake Ontario were obtained from a variety of sources. Bathymetric and daily meteorological data, used by Boyce et al. [4], were provided by Dr. Paul Hamblin at the Canadian Centre for Inland Waters (CCIW). Certain constants pertaining to lake dynamics were taken from Imberger and Patterson [21]. Initial Lindane concentrations for DYRESM-Ont were estimated from measurements taken during the month of April during the last decade (section 2.5.3), and daily air concentrations were calculated using the algorithm described in section 2.5.4.

2.5.1 Meteorological and Bathymetric Data for Lake Ontario

1972 - 1973 was the International Field Year on the Great Lakes (IFYGL), which focused on Lake Ontario. At regular intervals from April 11, 1972 through April 11, 1973, vertical temperature profiles were measured throughout Lake Ontario. A contour plot of these measurements, presented later in this chapter, provides a comparison for DYRESM's simulated temperatures. Additionally, meteorological conditions were recorded at many stations across the lake: wind speed was measured four times per day, the air temperature at a height of four metres above the lake's surface was taken daily, and radiative information was both measured and calculated to provide daily information. The averages of these meteorological inputs are graphically presented in figure 2.5. This data set is the most complete compilation of weather and temperature information available for Lake Ontario, and therefore is the most suitable choice for use with DYRESM. Although
there were a few extraordinarily heavy storms that year, it is considered reasonably typical, and this data has been used previously with DYRESM by Boyce et al. [4]. Both the bathymetric data for Lake Ontario and the meteorological data for 1972 - 1973 were provided by CCIW for use in this research.

Initial temperature and salinity conditions for the first day of the simulation, April 11, 1972, were taken at seven locations over the depth of the lake (table 2.1). These measurements were made during a period of thermal inversion, which accounts for the colder temperatures at the surface. This is expected to occur prior to spring turnover.
<table>
<thead>
<tr>
<th>Height (m)</th>
<th>Temperature (°C)</th>
<th>Salinity (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>238.31</td>
<td>1.50</td>
<td>230</td>
</tr>
<tr>
<td>178.31</td>
<td>1.55</td>
<td>230</td>
</tr>
<tr>
<td>148.31</td>
<td>1.75</td>
<td>230</td>
</tr>
<tr>
<td>118.31</td>
<td>2.15</td>
<td>230</td>
</tr>
<tr>
<td>88.31</td>
<td>2.50</td>
<td>230</td>
</tr>
<tr>
<td>63.31</td>
<td>2.65</td>
<td>230</td>
</tr>
<tr>
<td>38.31</td>
<td>2.70</td>
<td>230</td>
</tr>
</tbody>
</table>

Table 2.1: Initial temperature conditions for April 11, 1972 applied to DYRESM-Ont. Heights are measured from the lakebed. Provided by the Canadian Centre for Inland Waters (CCIW).

2.5.2 Constants

DYRESM requires specification of seven constants relating to lake dynamics, primarily for the heating and mixed layer algorithms. The values for these constants were determined by Imberger and Patterson [21], and have only been altered as noted:

- $C_d$, the drag coefficient for inflowing streams ($=0.015$). Used in equations 2.33 and 2.34.

- $\eta_1$, the extinction coefficient for short wave radiation penetrating below the surface ($=0.4$). Modified for Lake Ontario by Boyce et al. [4]. Used in equation 2.10.

- $\alpha_1$, a constant reflecting the percentage of surface energy which can be applied to hypolimnetic mixing ($=0.02$). Modified by Dr. Paul Hamblin [4] from Harleman's work [1]. Used in equation 2.28.

- $C_k$, a stirring efficiency coefficient for convective overturn in the mixed layer ($=0.125$). Used in equations 2.15 and 2.17.

- $\eta$, another stirring efficiency coefficient ($=1.23$). Used in equation 2.16.

- $C_s$, a coefficient of efficiency of shear production for entrainment of deeper waters into the mixed layer ($=0.2$). Used in equation 2.24.

- $C_t$, a coefficient of the temporal effects due to surface wind stress or cooling ($=0.510$). Used in equation 2.18.
### Table 2.2: Measured concentrations of Lindane in Lake Ontario, in $ng\ L^{-1}$. From sources as cited.

<table>
<thead>
<tr>
<th>Location</th>
<th>Dates</th>
<th>Mean Concentration</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>April 1986</td>
<td>1.376</td>
<td>L’Italien [27]</td>
</tr>
<tr>
<td></td>
<td>August 1986</td>
<td>1.310</td>
<td>McConnell et al. [35]</td>
</tr>
<tr>
<td></td>
<td>April 1988</td>
<td>0.872</td>
<td>L’Italien [27]</td>
</tr>
<tr>
<td></td>
<td>April 1990</td>
<td>0.549</td>
<td>L’Italien [27]</td>
</tr>
<tr>
<td></td>
<td>August 1990</td>
<td>0.370</td>
<td>McConnell et al. [35]</td>
</tr>
<tr>
<td></td>
<td>May 1993</td>
<td>0.336</td>
<td>Ridal et al. [44]</td>
</tr>
<tr>
<td></td>
<td>May - October 1993</td>
<td>0.360</td>
<td>Ridal et al. [43, 44]</td>
</tr>
<tr>
<td>Deep</td>
<td>August 1990</td>
<td>0.440</td>
<td>McConnell et al. [35]</td>
</tr>
<tr>
<td></td>
<td>May - October 1993</td>
<td>0.403</td>
<td>Ridal et al. [43, 44]</td>
</tr>
<tr>
<td>Niagara</td>
<td>Average 1993</td>
<td>0.4505</td>
<td>Kuntz [25]</td>
</tr>
</tbody>
</table>

#### 2.5.3 Concentration of Lindane in Lake Ontario

Measurements of Lindane concentration have been taken in Lake Ontario by a handful of research groups during the past decade [25, 27, 35, 43, 44]. There has been a noticeable decrease in the concentration of Lindane in the lake over the last ten years.

Measured Lindane concentrations for Lake Ontario and the Niagara River are presented in table 2.2. Measurements taken in April or May were used as the initial conditions for the DYRESM-Ont model, with a preference for the most recent values. For all simulations with the model DYRESM-Ont, an initial surface concentration of 0.32 $ng\ L^{-1}$ was used; Ridal et al. [44] had a value of 0.336 $ng\ L^{-1}$ for May 1993, and a slightly lower value for the colder month of April seemed appropriate. Measurements in deep waters were more difficult to obtain, and there were no data available for April, so a value of 0.40 $ng\ L^{-1}$ was deemed satisfactory. The daily inflow concentration was maintained at 0.4505 $ng\ L^{-1}$ [25].

#### 2.5.4 Concentration of Lindane in the Air above Lake Ontario

Since 1985, air concentrations of Lindane in the Great Lakes region have been found to range from around 10 $pg\ m^{-3}$ in the winter months to a mean of about 50 $pg\ m^{-3}$ in summer [17, 26, 35, 43, 44]. These concentrations have remained relatively constant during the last decade. Hoff et al. [17] measured atmospheric Lindane concentrations in Southern Ontario periodically during 1988 and 1989, and derived the following relationship for Lindane in the air over the Great Lakes:
Figure 2.6: Lindane concentration in the air above Lake Ontario. Left: Log-graph of air concentration vs. the inverse of air temperature with lines fit to the measured data. Right: Variation of concentration over time. A daily comparison of the results from equation 2.83 to measurements, with $m = -3200$. Air temperatures used in equation 2.83 are from the 1972/1973 IFYGL data.

$$\log C_a = b + \frac{m}{T}$$  \hspace{1cm} (2.83)

where $C_a$ is the air concentration in $pg m^{-3}$, $T$ is the temperature in °K. and $m$ and $b$ are constants, with $b = 12.6 \pm 0.2$ and $m = -3100 \pm 400$. An $r^2$ value of 0.44 was obtained by Hoff et al. [17] for this relationship.

When compared to a larger data set of measurements for the air above Lake Ontario taken by Lane et al. [26, taken 1985-1987], Ridal et al. [43, 44, taken in 1993], and McConnell et al. [35, taken 1986-1990], equation 2.83 was found to overpredict Lindane concentrations, especially in the summer. Figure 2.6 shows that when $m = -3200$ in equation 2.83, the temperature dependence of air concentration is more closely approximated, and computed concentrations using this $m$ match measured values reasonably well. Furthermore, the correlation coefficient for equation 2.83 with $m = -3200$ is $r^2 = 0.598$, which is an improvement over the findings of Hoff et al. [17]. Therefore, in DYRESM-Ont, the constants were set to $m = -3200$ and $b = 12.6$.

A linear regression analysis produced a line with constants $b = 10.6$ and $m = -2620.$ and a correlation coefficient of $r^2 = 0.683$. At the right side of figure 2.7, it can be seen that the differences between the air concentrations of Lindane predicted by these two equations are negligible. The new equation could be used in future simulations using DYRESM-Ont, however, a greater number of measurements would be beneficial in
Figure 2.7: Atmospheric Lindane concentration. Equation obtained by linear regression analysis: \( \log C = 10.6 - 2620/T \). Equation implemented in DYRESM-Ont: \( \log C = 12.6 - 3200/T \). Left: Log-graph of air concentration vs. the inverse of air temperature with lines fit to the measured data. Right: Variation of concentration over time. A daily comparison of the results from both equations. Air temperatures used in equation 2.83 are from the 1972/1973 IFYGL data.

determining a more precise linear regression fit.

2.6 Validation of the Model

DYRESM-Ont was validated for Lake Ontario by four main processes: temperature predictions were compared to known values; DYRESM's diffusion equations were matched to an analytical solution; the operation of GASTRANS was verified by comparing \( K_{tot} \) to other research results; and a baseline model for Lindane concentration predictions was created and verified against measured data. The baseline model is included in chapter 3 to facilitate comparison to the test scenarios which are presented there.

2.6.1 Temperature Predictions

A contour plot of Lake Ontario's temperature profile measurements for the IFYGL presented in figure 2.8, was taken from a study performed by Boyce et al. [4]. A year-long temperature profile for Lake Ontario was generated by DYRESM, using the IFYGL meteorological and bathymetric data (figure 2.9), and compared to the measured values.

While the simulated profile has fewer isotherms for clarity, the overall characteristics of the measured thermal structure are observed to have been reproduced quite well. Spring and fall periods of destratification, when the lake became well mixed, occur at the same
times in both plots. However, DYRESM predicted a deeper thermocline: the model’s $16^\circ C$ isotherm is about $20\text{ m}$ below the measured depth. The thermocline also appears to be about $10\text{ m}$ thicker in DYRESM’s temperature plot. Additionally, the simulation produced slightly lower surface temperatures, with less detail in the epilimnion, and slightly warmer deep temperatures. The largest variations in temperature occurred from October through December, with an increase of more than $4^\circ C$ at certain depths above measured values. In the late winter months, the isotherms were not accurately simulated, but the temperature predictions were within $1.5^\circ C$ at any given depth.

According to Hutter [20], the modelling of limnological processes is far from perfect, due primarily to the lack of understanding of the complex mechanics involved, and also because the applied meteorological forces are subject to statistical behaviour. Consequently, although the predicted temperature profile is not an exact match to the measured values, DYRESM was considered to have simulated the lake mixing processes sufficiently well for use in this project.
2.6.2 Diffusion Subroutines

In the hypolimnion, molecular diffusion is considered to be the primary mechanism for chemical dispersion (refer to section 2.2.3). Diffusive processes are modelled by the subroutines FCT and DIFUSE for both heat and mass transport.

Simplified inputs, such as zero windspeed and constant surface temperature, were applied to DYRESM-Ont to simulate a case of pure diffusion, for both temperature and concentration. The daily results from these test runs were compared to an analytical solution, presented in appendix A.

The numerical predictions and the analytical solution after 100 days are compared in figure 2.10 for both heat and mass. In both cases, the curves matched almost exactly. A more detailed examination demonstrated that the similarity improved as time passed. All conservative tracers, irregardless of units of concentration or initial conditions, produced identical curves.

2.6.3 Gas Transfer Velocity

A simplified version of the GASTRANS subroutine was run and compared to a variety of measured results for a chemical with a Schmidt number $Sc_w = 600$, to represent carbon dioxide. The wind speed was varied linearly, while all other inputs were held constant.

Figure 2.11 shows the variation between the measured data and the model's values. DYRESM-Ont matches all but Donelan and Drennan's results [7] very well below wind
Figure 2.10: Variation of tracer concentration with depth: A comparison of diffusion subroutines and analytical solutions of the diffusion equation for heat (top) and mass (bottom) after 100 days, with diffusivity $= 10^{-6} \text{ m}^2 \text{s}^{-1}$ in both cases. For the temperature plot, $T_i = 10^\circ C$ and $T_o = 20^\circ C$. For the concentration plot, $C_i = 0 \text{ ng L}^{-1}$ and $C_o = 350 \text{ ng L}^{-1}$.
Figure 2.11: Gas transfer velocity vs. windspeed: Comparison of DYRESM-Ont's results for $K_{tot}$ against experimental results. Based on the laboratory work of Ocampo-Torres et al. [37], field measurements made by Donelan and Drennan [7], and dual tracer studies by Watson et al. [49] and Wanninkhof et al. [48]. All results normalized to $Sc_w = 600$. Plot modified from Hancock [13].

speeds of 10 m s$^{-1}$. At higher wind speeds, it is much closer to their field measurements, but quite a bit higher than the results from the laboratory measurements and dual tracer studies. In general, it seems to be reasonably accurate at higher wind speeds. Considering the discrepancies between the other studies, and very accurate at medium to low wind speeds, which is encouraging, since the input data for Lake Ontario has wind speeds which are as high as 15 m s$^{-1}$, but are generally less than about 12 m s$^{-1}$. 
Chapter 3

Results and Discussion: Test Scenarios

The efficacy of DYRESM-Ont as a predictive tool was investigated for several situations, and the results of the simulations were examined. The first scenario was a baseline simulation, which used the input data described in the previous chapter. The results were compared to known concentrations to judge the accuracy of DYRESM-Ont. The predictions of the hypothetical scenarios were then compared to the concentration profiles simulated by this baseline model.

Lindane, although not currently used in agricultural applications in Canada or the United States, has historically been sprayed over crops. This spraying tended to cause an increase in Lindane concentration in the air over Lake Ontario during the spring, a phenomenon which still occurs to a lesser degree as a result of global atmospheric transport of Lindane used in Central America and the Caribbean [17]. Seasonal fluctuations in Lindane concentrations over Southern Ontario have been measured by Hoff et al. [17], and these are reflected in the case studies. The effects of different scenarios which could cause increases in $C_a$ were examined. The scenarios include a doubling in atmospheric concentration, the effects of global climate change, multi-year simulations which model spring-time crop spraying, and a reduction of the gas transfer velocity.

There were no measured concentrations of Lindane in Lake Ontario available for the hypothetical situations, so the initial concentrations were maintained at the baseline values given in section 2.5.3. A start-up period was expected to occur at the beginning of each simulation while equilibrium was established in the lake.
Figure 3.1: Height vs. time contour plot of predicted Lindane concentrations in Lake Ontario for the baseline simulation. Concentrations are given in \(ng \, L^{-1}\).

### 3.1 Baseline Simulation for Concentration Predictions

A baseline simulation to predict the concentration of Lindane in Lake Ontario was performed, using the data described in section 2.5. The resulting daily concentration profile, presented in figure 3.1, shows concentration contour lines that are similar to the isotherms from the temperature profile (figure 2.9). This is expected, since mass is known to be transported by the same processes as heat [10]. In the concentration profile, Lindane appears to undergo a form of stratification during the same months as temperature stratification, and in both graphs, there is more activity during the summer than the winter. The corresponding stratification of Lindane is referred to as concentration stratification in this thesis. The concentrations are highest in the summer, which indicates deposition during the warmer months and volatilization during the colder season.

More detailed plots of the summer months are given in figure 3.2, when the lake was stratified. Stratification began in early June, and the mixed layer was starting to deepen to the bottom of the lake at the end of September. Very steep concentration gradients can be seen at the location of the thermocline during these warmer months, and the deeper waters remained at 0.4 \(ng \, L^{-1}\) for this period.

To validate the predictions made by DYRESM-Ont for Lake Ontario, the simulated concentrations were compared to the field measurements compiled in section 2.5. As
Figure 3.2: Predicted daily contour plots of Lindane concentration as a function of height above the lakebed for the Lake Ontario baseline simulation during the summer months. Concentrations are given in ng L$^{-1}$. 
mentioned previously, the available data has a high variance because Lindane measurements were taken infrequently, and at a variety of locations. Also, many testing stations are near the shore of the lake, where emissions from industrial sites or spraying in agricultural regions can cause varying measurements. For example, the surface concentrations of Lindane in Hamilton Harbour were higher than $10 \text{ ng} \text{ L}^{-1}$ in April 1988 and 1990 [27], while in the rest of the lake, $C_w$ at the surface ranged from around $0.300 \text{ ng} \text{ L}^{-1}$ to no higher than $1.300 \text{ ng} \text{ L}^{-1}$ [27, 35, 44] during the month of April, 1986 to 1993.

Maximum measured concentrations of Lindane in the surface waters of Lake Ontario during the summers of 1990 and 1993 were found to be just over $0.40 \text{ ng} \text{ L}^{-1}$ [35, 43, 44], while McConnell et al [35] measured concentrations up to $1.31 \text{ ng} \text{ L}^{-1}$ in August 1986. DYRESM predicted values close to the most recent measurements, with an average surface concentration of around $0.50 \text{ ng} \text{ L}^{-1}$. A spike of $0.60 \text{ ng} \text{ L}^{-1}$ occurred for five or six days towards the end of July (see figure 3.2), and then returned to the average of $0.50 \text{ ng} \text{ L}^{-1}$. The simulation’s predicted surface concentrations for the spring and fall closely matched measured concentrations of around $0.33 \text{ ng} \text{ L}^{-1}$ in April and October [27, 35, 43, 44]. Unfortunately, field data for the winter surface concentrations were unavailable. The predicted concentrations in the surface layer fluctuated in the summer, but were relatively constant in the winter (figure 3.3).

Deep water measurements were scarce and no data was available for the winter months. The plot of the daily concentration at a height of $5 \text{ m}$ (figure 3.3) shows that DYRESM-Ont placed the summertime deep water concentrations just below $0.40 \text{ ng} \text{ L}^{-1}$. Measurements made in the deeper waters from May through October 1993 found a concentration of $0.403 \text{ ng} \text{ L}^{-1}$ [44], and in August 1990, the value was a bit higher, at $0.440 \text{ ng} \text{ L}^{-1}$. The deep water concentration was constant until December, when it dropped to less than $0.25 \text{ ng} \text{ L}^{-1}$, reflecting the mixing over the depth during the colder months.

Figure 3.3 displays the variations in Lindane concentration in four different layers over the year. Near the bottom of the lake, it is apparent that no changes in concentration occurred while the lake was stratified, and there was a decrease during the winter. once Lake Ontario became fully mixed. At a height of $150 \text{ m}$, there was little change in concentration during the summer months of stratification, but this period of constant concentration was much shorter than for the deep waters, because the upper layers were mixed earlier. The plot of the waters near the surface at a height of $200 \text{ m}$ demonstrates many similarities to the uppermost layers over the entire year. The concentration varies throughout the summer on a daily basis, and decreases and becomes less variable during the winter months. The surface layer has the highest concentrations. In all four plots, the highest values occur during the summer months ($0.6 \text{ ng} \text{ L}^{-1}$ for the surface layer
Figure 3.3: Variation of Lindane concentration over time in Lake Ontario (baseline simulation) at various heights above the lakebed.

and 0.4 ng L\(^{-1}\) for the bottom layer), and the lowest concentrations are found during the winter (0.25 ng L\(^{-1}\) for all layers).

In general, DYRESM-Ont predicted concentrations that were similar to the available measured values. To fully validate this model, more extensive measurements of Lake Ontario’s temperature and Lindane concentrations would have to be gathered.

DYRESM-Ont has shown that air-water gas exchange is an important transport process for Lindane in Lake Ontario. With only surface gas exchange and river inflow as chemical input mechanisms, the predicted values were similar to measured values. Typical Lindane inputs from the Niagara River were approximately 0.25 kg d\(^{-1}\). The magnitude of the gas flux through the surface was approximately 10 – 100 times larger than the Niagara River flux.

It is expected that deposition of Lindane into the surface of Lake Ontario occurs in
the late spring and early summer, when the air concentration is high, but the water temperature is low, which increases the solubility; volatilization is likely to occur as the air temperature cools (decreasing the concentration), but the water is still fairly warm, in the early autumn [3]. DYRESM-Ont predicted an average daily surface flux into Lake Ontario of approximately $0.1 \, ng \, m^{-2} \, d^{-1}$ from April until the beginning of September. From September through January, the predicted flux was out of the lake with an average value of $0.2 \, ng \, m^{-2} \, d^{-1}$. The net annual flux was into the lake and had a value of $0.01 \, ng \, L^{-1}$, which represents a mass of about $50 \, kg \, y^{-1}$.

McConnell et al. [35] estimated an outward flux of $5.1 \, ng \, m^{-2} \, d^{-1}$ during August 1993. However, in their simulation, the air concentration in August was much lower than either July or September, which is not in keeping with the findings of Lane et al. [26] and Hoff et al. [17]. Additionally, the water temperature was set higher in August than in any of the other months. These factors would account for the prediction of a dramatic loss of Lindane into the atmosphere. However, McConnell et al. [35] suggest that although Lindane appears to volatilize from the Great Lakes during the late summer, the net annual flux is likely depositional [35]. In a study by Ridal et al. [44], net deposition of around $2.6 \, ng \, m^{-2} \, d^{-1}$ of Lindane to Lake Ontario was measured from May through October 1993, for a total transfer of 37 $kg$ over the summer months. DYRESM-Ont predicted a net deposition of approximately 60 $kg$ during this same time. Ridal et al. [44] found that surface gas exchange is the dominant mechanism of Lindane transport in Lake Ontario from May through October. Mass transfer resulting from gas transfer was more than double the transport via the Niagara River and precipitation. It is generally agreed that air-water gas exchange does play an important role for Lindane in Lake Ontario, and is of the same or higher order as wet deposition [35, 44].

### 3.2 Elevated Atmospheric Lindane Concentration

When atmospheric Lindane concentration ($C_a$) was plotted against Lindane concentration in Lake Ontario ($C_w$) for the baseline model, a linear relationship was observed (figure 3.4. A greater abundance of chemical in the atmosphere will cause more deposition to the surface waters. An increase in air concentration is therefore expected to proportionally increase the overall deposition of Lindane to Lake Ontario, causing higher overall water concentrations.

To model the effect of an increase in the atmospheric Lindane concentration, the magnitude of $C_a$ (predicted by equation 2.83) was increased by a factor of two. This simulated a summertime average $C_a$ of approximately $100 \, pg \, m^{-3}$ instead of the baseline
Figure 3.4: Concentration of Lindane in surface water vs. atmospheric concentration for baseline simulation.

value of 50 pg m$^{-3}$. All other data, including initial concentrations, were maintained at the same values as in the baseline simulation.

The resulting concentration profile, figure 3.5, demonstrates a pattern of contour lines similar to the results from the baseline simulation, with about a two-fold increase of surface concentration $C_w$. Surface water concentrations peaked at 1.2 ng $L^{-1}$ in this model in July. During the same month in the baseline model, the peak value was only 0.60 ng $L^{-1}$. It is interesting to note that the April and August 1986 surface concentrations presented in table 2.2 are 1.376 and 1.310 ng $L^{-1}$ respectively, which may have been the result of a higher atmospheric Lindane concentration during that year.

Daily concentrations for the surface layer, the bottom layer, and two intermediate layers are presented in figure 3.6, with comparisons to the baseline concentrations. Fluctuations in concentration are intensified in the high concentration simulation. The initial water concentrations were kept at the same values as in the baseline simulation. Therefore, a start-up adjustment period was expected to occur while the lake established equilibrium. As shown in these plots, after about one month, the concentration in all layers was approximately double the baseline simulation's values.

A graphical comparison of the surface and deep water concentrations between the present simulation and the baseline model (figure 3.7) displays a 50 day start-up period (until about June 1), during which time the lake attempted to equilibrate and to compensate for the increased flux into the surface. Once the lake became stratified, the surface
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Figure 3.5: Height vs. time contour plot of Lindane concentration in Lake Ontario with doubled $C_a$. Concentrations are given in ng L$^{-1}$.

Concentration ratio stabilized at around 1.95 for the remainder of the simulation, while the deep water concentration was almost 1.7 times that of the baseline model. The deep water ratio was maintained for the entire period of stratification. In September, when the mixed layer deepened to the lakebed, this ratio increased to 2. These results indicate that some vertical mixing occurred prior to springtime stratification, which increased the deep water concentration considerably. Once the lake became stratified, there was no mass transport from the surface layers to the bottom-most layer until destratification in the autumn, when the extra chemical was distributed throughout the depth of the lake.

An analytical comparison between the baseline model and the elevated atmospheric concentration model was performed, to more closely examine the proportionality between $C_a$ and $C_w$. For any given day in both simulations, $K_{tot}$ and the supersaturation term $(1 + \Delta)$, which are dependent on chemical and meteorological properties, were considered identical. The two fluxes (from Hancock [13]), $F_1$ for the baseline model and $F_2$ for the increased $C_a$ model, were given as:

\[
F_1 = K_{tot}(\beta(1 + \Delta)C_a - C_{w1}) \quad (3.1)
\]

\[
F_2 = K_{tot}(\beta(1 + \Delta)(2)C_a - C_{w2}) \quad (3.2)
\]

where $C_{w1}$ and $C_{w2}$ represent the Lindane concentrations in the water for the baseline model and the increased $C_a$ model respectively.
Figure 3.6: Variation of Lindane concentration over time in Lake Ontario at various heights above the lakebed for baseline model and elevated $C_a$ simulation.
Figure 3.7: Ratio of Lindane concentrations between the doubled $C_a$ model and the baseline simulation. Top: Ratio of surface water concentrations. Bottom: Ratio of deep water concentrations.

The smaller supersaturation terms were neglected, and after some manipulation, an equation for the ratio of $C_{w1}$ to $C_{w2}$ was obtained.

$$\frac{C_{w2}}{C_{w1}} = 2 + \frac{1}{K_{tot}C_{w1}}(2F_1 - F_2) \tag{3.3}$$

Since the air-water boundary is generally close to an equilibrium state, it is reasonable to suppose that a doubling of $C_a$ would cause the flux to increase by a similar proportion. Thus, the term $2F_1 - F_2$ in equation 3.3 could be considered small, producing a concentration ratio of around 2 for this scenario. As figure 3.7 shows, the ratio between surface concentrations is 1.95, which demonstrates that the second term in equation 3.3 does play a small role, with $F_2$ slightly greater than twice $F_1$.

Although the atmospheric Lindane concentration was quite high at times in the past [27], it is unlikely that there will be a doubling of Lindane in the air above Southern Ontario in the future. By law, Lindane is no longer used in North America, and is only transported in trace quantities in the atmosphere from Central and South America [17]. Also, Hoff et al. [17] suggest that Lindane can be volatilized from the surface of the earth under certain conditions, including an increase in ambient air temperature. The result of such a temperature increase could cause a dramatic rise in $C_a$ and thus $C_w$, but the lake’s concentration would still remain below most water quality limits, which vary but
are typically between 5 and 10 \( ng \, L^{-1} \) [41]. In this simulation, the concentration did not exceed 1.3 \( ng \, L^{-1} \) anywhere in Lake Ontario. The best application of this particular simulation would be to investigate historical Lindane concentrations in Lake Ontario when the atmospheric concentration was greater (refer to table 2.2).

### 3.3 Global Climate Change Scenario

A previous study of Lake Ontario which used DYRESM investigated the effects of climate change due to a doubling of atmospheric Carbon Dioxide (CO\(_2\)), the dominant greenhouse gas, on the structure of the lake’s temperature profile [4]. DYRESM-Ont was run with the modified meteorological conditions used in the afore-mentioned study, to examine the results of a global climate change scenario on the concentration profiles of Lindane in Lake Ontario.

Boyce et al. [4] compiled data from both regional and Global Circulation Models of the atmosphere, to approximate the effects of a doubling of atmospheric CO\(_2\). The resulting changes to the meteorological data, shown in table 3.1, were applied to DYRESM-Ont. The affected variables, estimated on a monthly basis, include air temperature, vapour pressure, wind speed, and cloud cover. Apart from these four variables, all input data remained unchanged, including the initial concentrations, which were not altered from the baseline model values.

The increase in air temperature as a result of global warming is graphically presented at the top of figure 3.8. This increase directly affected the air concentrations, shown at the bottom of the same figure, which were calculated using equation 2.83.

Temperatures in this case differed from the baseline temperatures, as shown in the temperature profile for the global warming scenario (figure 3.9). The thermocline appears steeper than in the baseline model, and occurs at a slightly lower depth. Overall, the temperatures were higher by about 4°C in this simulation. Also, the annual range of water temperatures was much smaller in the elevated \( C_a \) model, due to an atmospheric warming from January through April of an average 8°C, with a maximum increase of 11°C in February in the climate change scenario. As a result of the late winter warming combined with a reduction in wind speed from January through April, annual stratification was expected to occur sooner in the springtime. Earlier lake overturn is apparent in the concentration profiles, which are given for the full year in figure 3.10, and in detail for the warmer months in figure 3.11. Stratification can be seen to occur midway through May in the climate change scenario (refer to figure 3.11), almost a month earlier than in the baseline model. Additionally, complete destratification was delayed
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Table 3.1: Changes applied to meteorological input data used in DYRESM-Ont for a global climate change scenario. Column A: Increase in air temperature (°C). B: Vapour pressure change (multiplying factor). C: Wind speed change (multiplying factor). D: Change in fractional cloud cover (additive factor). Values given are monthly averages, taken from Boyce et al [4].

Figure 3.8: Daily comparison between baseline simulation and global climate change scenario input variables. Top: Variation of air temperature over time. Bottom: Variation of atmospheric Lindane concentration over time.
Figure 3.9: Predicted daily temperature contours plotted as a function of height above the lakebed for Lake Ontario under global climate change scenario. Temperatures are given in °C.

by about a week at the end of December (figure 3.10).

In the climate change model, the concentrations along similar contours were typically greater than the baseline model concentrations by around 0.1 ng L\(^{-1}\), with the exception of January through March, where the concentrations rose by more than 0.2 ng L\(^{-1}\) to 0.5 ng L\(^{-1}\) at the surface in March. The maximum Lindane concentration occurred towards the end of July, with a value of 0.68 ng L\(^{-1}\) in the surface layers, as can be seen in figure 3.11. From January to March, the number of contour lines increased dramatically, reflecting the increase in \(T_a\), which caused a higher \(C_a\). In other words, constantly varying air concentrations effected frequent changes to the Lindane concentration in the water. A plot of the concentration at several depths (figure 3.12) shows a start-up phase of around 50 days, as in the high concentration scenario. After this initial phase, the most noticeable effects of climate change occurred during stratification in the deeper waters, where the concentration was higher than the baseline model’s by approximately 0.1 ng L\(^{-1}\). From May to December, the deep water concentration was maintained at 0.55 ng L\(^{-1}\). The most dramatic difference over the entire depth happened after January, as a result of the most radical alterations to the meteorological inputs; concentrations nearly doubled in all layers.

The effects of global warming were examined by plotting the ratio between the concentrations predicted in the climate change scenario and the baseline simulation, for the
surface and bottom layers (figure 3.13). At the top of the figure, the plot of the concentration ratio in the surface layer indicates that concentration increased by 50% in April, 20% in the summer months, and between 50% and 100% from January through March. A plot of the ratio of the predicted deep water concentrations is presented at the bottom of the same figure. Deep water concentration increased by 50% in April, 40% throughout the summer, 100% when the lake was unstratified, and between 50% and 100% from January through March. During the summer months, stratification prevented any significant variation in concentration in the surface layer. At the same time, the deep water concentration was a constant 40% greater than the baseline value. The mixed layer deepened at the same time as the most significant changes in atmospheric conditions, near the end of December. Just before the epilimnion entrained the bottom layer, the ratio between deep water concentrations increased dramatically, to more than 200%. This occurred because at this time in the baseline simulation, the lake had already become mixed, so the bottom layer had attained its lower concentration. As the lake became fully mixed in the climate change scenario, the deep water concentration suddenly decreased, as did the concentration ratio between the two scenarios. The higher winter air temperatures caused a proportional increase in both the surface water and the deep water concentration of Lindane during the winter and early spring months, because the lake was fully mixed over this time.
Figure 3.11: Predicted daily Lindane concentration contours plotted as a function of height above the lakebed for the Lake Ontario global climate change scenario during the warmer months. Concentrations are given in \( ng \, L^{-1} \).
Figure 3.12: Variation of Lindane concentration over time in Lake Ontario at various heights above the lakebed. Comparison of climate change scenario to baseline simulation.
Figure 3.13: Lindane concentrations in Lake Ontario: ratio of baseline simulation to global climate change scenario. *Top:* Ratio of concentrations in the surface layer. *Bottom:* Ratio of concentrations in the bottom layer.

The occurrence of stratification in Lake Ontario, as it relates to chemical concentrations, can be seen in a plot of the concentrations on several single days (figure 3.14). On all the days plotted, the concentration was higher at all depths in the climate change simulation. On June 1, the surface mixed layer was just beginning to form in the climate change model; however, in the baseline simulation, it had not yet begun to form. The concentration was about 0.15 $\text{ng} \text{L}^{-1}$ greater at all depths in the climate change scenario. In the plot for July 20, concentration stratification is clearly present in both simulations. With higher concentrations in the new model. In the surface waters, the concentration is greater by approximately 0.1 $\text{ng} \text{L}^{-1}$, and in the deeper waters, by approximately 0.15 $\text{ng} \text{L}^{-1}$. On September 8, the surface layer was evident in both simulations, but the variation of concentration with depth was half as large in the climate change scenario. The concentration was greater in the climate change model by approximately 0.15 $\text{ng} \text{L}^{-1}$ in the deeper waters, and by approximately 0.1 $\text{ng} \text{L}^{-1}$ in the surface waters. The deep water concentration was greater than the surface concentration by October 29, by a larger increment than in the baseline simulation. By this time, destratification (fall turnover) had begun to occur, but the climate change simulation experienced turnover later, and its surface layer was 25 $m$ shallower. As the mixed layer deepened towards
the bottom of the lake, the concentration in the surface waters decreased. This resulted from warm surface water temperatures, and correspondingly lower Lindane solubility, with lower atmospheric Lindane, resulting from colder autumnal air temperatures. On average, concentrations were about 0.1 ng L$^{-1}$ greater in the climate change scenario than in the baseline simulation.

DYRESM-Ont predicts that the effects of global climate change would cause an increase in Lindane concentration in Lake Ontario. The most dramatic increases would occur during the late winter and early spring, when the air concentrations would be the most elevated. The atmospheric changes would also hasten the onset, and extend the duration of the period of stratification.

### 3.4 Long-term Simulation: Baseline Inputs

In the field of environmental modelling, it is useful to be able to provide predictions over several years, or even decades. DYRESM-Ont was run for four years, using the
Figure 3.15: Predicted daily Lindane concentration contours as a function of height above the lakebed for the four-year Lake Ontario baseline simulation. Concentrations are given in ng L⁻¹.

The same baseline model data each year, to determine its long-term capabilities. The original initial conditions were applied to the first day of the first year of the simulation only, and daily computed concentrations were used as inputs for each following day. At the end of every year, DYRESM-Ont looped back to the beginning of the baseline daily data files.

The long-term baseline model concentration profiles presented in figure 3.15 indicate nearly identical annual results. Contour lines occur in the same locations, for the same concentrations, at the same times in consecutive years. This demonstrates that there are no errors building up in DYRESM-Ont that could create modelling difficulties over multi-year runs.

A start-up period can be seen during the first month of the first year, when the initial conditions imposed a concentration of between 0.32 and 0.40 ng L⁻¹, but this is not present during the other years, when a uniform concentration of 0.3 ng L⁻¹ occurred.
at the beginning of the year (in the middle of April). Thus, it was concluded that the initial concentrations were set a little too high, and the lake took around 50 days to reach an equilibrium state. After the first start-up period, the plots were practically the same every year.

This simulation demonstrated DYRESM-Ont's ability to operate consistently over an extended period of time, and provided a set of long-term baseline concentrations against which results from further scenarios could be evaluated.

3.5 Long-term Simulation: Spraying of Lindane

The long-term effects of pesticide and herbicide spraying are of concern in the Lake Ontario region. Annual springtime agricultural applications of certain chemicals increase the local air concentration, which has a direct impact on the concentrations in the lake [17, 35]. Although Lindane itself is no longer used locally, it is representative of the group of organochlorine pesticides which are still in use in the Great Lakes region.

To model the effects of Lindane spraying, the air concentration was doubled for a brief period in either the spring or early summer. In the first situation, $C_a$ was doubled for two weeks in April of the second year (April 11 through 25). In the second case, spraying was modelled as occurring for almost three months in the first year, beginning on April 11 and ending on June 30. The resulting concentration profiles are presented in figures 3.16 and 3.20 respectively.

Two-Week Spraying in Year 2

$C_a$ was doubled for the first two weeks of the second year of this simulation. Performing a multi-year simulation for this test seems to have been unnecessary. According to the concentration profile data, the lake had fully recovered by the middle of December of the second year. After that time, the concentration profiles match the baseline model profiles. The effects of the two-week spraying can best be seen in figure 3.17, which shows the effects of the increased Lindane at different depths during the second year. The lake had not yet begun to experience stratification by the time the 50 day start-up period was finished, and the extra chemical injected into the surface was completely mixed vertically. The surface concentrations differed only marginally from the baseline model throughout the stratified period, while the deeper water concentrations increased by about 0.1 ng L$^{-1}$. The concentration ratio between the baseline model and the Lindane spraying model are plotted in figure 3.18 for the uppermost layer and the bottom layer. The surface layer's
Figure 3.16: Predicted daily Lindane concentration contours \( (ng \ L^{-1}) \) for Lake Ontario plotted as a function of height above the lakebed. Scenario: two-week spraying occurring from April 11 through April 25 in Year 2.
Figure 3.17: Variation of Lindane concentration over time in Lake Ontario at various heights above the lakebed for Year 2 of the first Lindane spraying scenario, with comparison to baseline simulation.

ratio is approximately unity after the start-up period for the duration of the simulation, while the deep water ratio is close to 1.25 during stratification, and just above unity after the lake experienced complete vertical mixing, also known as fall turnover.

Concentration plots for single days are presented in figure 3.19. On June 1, the lake has not yet become stratified, and the concentration is greater than in the baseline model over the entire depth, by about 0.1 ng L$^{-1}$. On the other days, the lake is stratified, and although the surface concentration is the same in both the spraying simulation and the baseline model, the deeper water concentrations are still larger by approximately 0.1 ng L$^{-1}$.

Lake Ontario has a residence time of six years for water. However, if chemicals enter and exit the upper layers before complete mixing occurs, the lake could be expected to recover from transient events more rapidly. Removal of Lindane via outflow and
through volatilization occurred rapidly enough in this simulation to restore the lake to normalcy within eight months of the spraying. The bulk of excess Lindane withdrawn from the lake was removed from the surface layer during stratification: as the uppermost waters equilibrated with the atmosphere, concentrations similar to the baseline surface values were quickly attained. The St. Lawrence River withdraws water with the same concentration as the surface layer, but this typically corresponds to a mass flux of much less than $0.1 \text{ kg d}^{-1}$ [42]. However, air-water transfers were responsible for fluxes from 5 to 50 $\text{kg d}^{-1}$. Once Lake Ontario became fully mixed, the Lindane which had been trapped at the bottom was available for transport into the atmosphere, and equilibrium concentrations were quickly attained.

**Multi-month Spraying in Year 1**

In this scenario, the spraying was assumed to cause a two-fold increase in $C_a$ from mid-April until the end of June of the first year. As expected, the application of Lindane for a longer period of time caused greater alterations in the concentration profile when compared to the long-term baseline model. While the spraying was occurring, concentrations were double the baseline values, such that there was a surface concentration of 0.9 $\text{ng L}^{-1}$ at the end of June. 50 $m$ below the surface, the concentration was higher than
Figure 3.19: Concentration of Lindane vs. height above the lakebed for Lake Ontario on individual days as indicated. Comparison between Lindane spraying scenario and baseline simulation.
CHAPTER 3. RESULTS AND DISCUSSION: TEST SCENARIOS

Figure 3.20: Predicted daily Lindane concentration contours as a function of height above the lakebed for Lake Ontario. Scenario: multi-month spraying occurring from April 11 through June 30 in Year 1. Concentrations given in $ng \, L^{-1}$. 
the surface concentration during stratification, until the end of August.

In a more detailed plot of the summer months of Year 1 (figure 3.21), it is evident that the mechanism of surface withdrawal had a significant impact on concentration profiles during the stratified period. Once the air concentration returned to normal values, the uppermost layer experienced a marked loss of Lindane, reducing the surface concentration to a near-equilibrium concentration of 0.5 ng L\(^{-1}\). However, at a depth of around 50 to 60 m below the surface, a pocket of higher concentration persisted. At this depth, the concentration was not reduced below 0.7 ng L\(^{-1}\) until October. Figure 3.22 shows some interesting daily concentration profiles. The bulge of high concentration in the layers beneath the surface is most apparent in July, but the effects lingered through September. At this time, the deep water concentration was almost 0.3 ng L\(^{-1}\) higher than in the baseline model, while the surface concentration was essentially unaltered. As the mixed layer began to deepen in October, the upper layers had a slightly higher concentration compared to the baseline model as the Lindane from the deeper waters was vertically dispersed. At the same time, the bottom layers continued to experience much higher concentrations than the upper layers.

As in the two-week spraying simulation, destratification caused almost instantaneous lake recovery in this scenario, as the concentrations returned to baseline values. In the full year contour plot, it appears that the lake was not fully back to normal until April of the following year. However, by examining the individual layers (figure 3.23), it can be seen that the concentrations in the baseline model and in the multi-month spraying simulation are almost identical by the end of December in Year 1.

According to the predictions of DYRESM-Ont, the effects of a two-and-a-half month doubling of Lindane input into the lake would be negligible six months after the cessation of spraying. The quick recovery of the lake in this simulation was due to Lindane's high solubility. The surface layer rapidly equilibrated with the atmosphere, and any Lindane trapped below the thermocline was transported to the surface when the mixed layer deepened during fall turnover. At that point, the entire water column was quickly brought to equilibrium with the atmosphere.

3.6 Summary

The goal of this research was to investigate air-water gas exchange and its effect on vertical concentration variations in a lake. The Dynamic Reservoir Simulation Model (DYRESM), which simulates mixing mechanisms in lakes and reservoirs and predicts vertical temperature variations, was modified to include subroutines for gas transfer
Figure 3.21: Predicted daily Lindane concentration contours as a function of height above the lakebed for Lake Ontario during the summer months in Year 1. Scenario: multi-month spraying occurring from April 11 through June 30 in Year 1. Concentrations given in ng L$^{-1}$. 
Figure 3.22: Concentrations of Lindane vs. height above the lakebed in Lake Ontario for individual days as indicated. Comparison between the two-week Lindane spraying simulation and the baseline simulation.
Figure 3.23: Variation of Lindane concentration over time in Lake Ontario at various heights above the lakebed for Year 1 of the multi-month Lindane spraying scenario, with comparison to baseline simulation concentrations.
processes in Lake Ontario, and renamed DYRESM-Ont. Chemical pathways include the inflowing Niagara River, epilimnetic and hypolimnetic mixing within the lake, the outflowing St. Lawrence River, and air-water gas exchange across the surface of the lake. Concentrations of Lindane, a highly soluble organochlorine pesticide that is both prevalent and persistent in the environment, were investigated. A baseline simulation was performed using bathymetric and meteorological data for the International Field Year on the Great Lakes 1972-1973. Concentrations of Lindane measured at Lake Ontario over the past decade were used as inputs to this model, and provided a basis for determining the accuracy of the model's predictions. The results from this baseline simulation were compared to the concentrations obtained from several case studies. These included a situation with elevated air concentrations, a global climate change scenario, and two instances of simulated springtime crop spraying.

It would have been preferable to have more measured data for comparison to the predicted concentrations. However, from the data available, it can be said that the predicted concentrations were similar to the most recent measurements. DYRESM-Ont computed Lindane concentrations of approximately 0.5 ng L\(^{-1}\) in the surface waters during the summer months, when the lake was stratified, and approximately 0.1 ng L\(^{-1}\) in the deeper waters at the same time. These values compare favourably with measured summertime concentrations of 0.4 ng L\(^{-1}\) in 1990 and 1993. In the winter Lake Ontario became unstratified, and DYRESM-Ont predicted concentrations of 0.35 ng L\(^{-1}\) throughout the lake.

From April through September, the total flux through the surface of the lake was from the air into the water, and an average of 0.1 ng m\(^{-2}\) d\(^{-1}\) was predicted. This estimate corresponds with the measurements of Ridal et al. [44], but differs from the predictions of McConnell et al. [35], who determined the flux over this time to be primarily the result of volatilization. From October through January, the direction of flux was determined to be towards the atmosphere. During the colder months, volatilization was expected to occur as a result of slightly warmer water temperatures, which corresponds to a lower solubility for Lindane, and because of reduced air concentrations. Lindane mass transport across the air-water interface was one to two orders greater than the amount of chemical entering the lake daily via the Niagara River, indicating the relative importance of the role of surface exchange of soluble gases in Lake Ontario.

A start-up period of approximately 50 days was identified, during which time the model established equilibrium and adapted to the atmospheric inputs. The accuracy of initial conditions was therefore found to be of little importance. This was especially evident in the test scenarios, for which no initial conditions were available; DYRESM-Ont
was found to be more heavily influenced by environmental conditions and Lindane concentration in the air over the course of the simulation than by the initial concentrations.

A two-fold increase of Lindane concentration in the air above Lake Ontario resulted in a doubling of concentrations in the lake. Whereas the concentration in July at the surface had been $0.6 \text{ ng L}^{-1}$ in the baseline model, in this simulation, the value was $1.2 \text{ ng L}^{-1}$ in the same location, at the same time. After the 50 day start-up phase, a ratio between the concentrations from the baseline model and the elevated concentration model was determined for both the surface layer and the bottom layer. The ratio at the surface was approximately 1.95 for the entire year-long simulation. For the bottom layer, the ratio between models was around 1.7 while the lake was stratified, and rose to 2 after lake overturn had occurred. In general, DYRESM-Out predicted that the increase in concentration of Lindane in water would be proportional to the increase in atmospheric Lindane concentration, due to its high solubility.

Global climate change due to a doubling of atmospheric carbon dioxide was simulated by altering the daily air temperature, vapour pressure, wind speed and cloud cover, based on the results of Global Circulation Models. The revised inputs changed the temperature structure in the lake, by deepening the mixed layer during the warmer months, and by lengthening the period of stratification. The most dramatic changes to the input meteorological data were made for the winter months, which caused a near doubling in concentrations over the depth of the lake, to a maximum of $0.5 \text{ ng L}^{-1}$ at the surface in March, compared to $0.3 \text{ ng L}^{-1}$ in the baseline simulation. In the summer months, the surface concentrations were higher than the baseline model's by about 20%, and the deep water concentrations were approximately 50% higher.

A multi-year simulation provided consistent results over four years when given identical annual meteorological input data, with the baseline initial concentrations and temperatures applied to the first day of the simulation only. Springtime Lindane spraying was modelled for two situations: a spraying period of two weeks, and a spraying period and two and a half months. In both cases, the spraying caused an immediate increase in the concentration of Lindane in the water. However, six months after the cessation of spraying, the lake had returned to the baseline concentration values. Lake Ontario's residence time for water is six years, but chemicals added at the surface were removed from the lake much more quickly. This is the result of chemical removal from the surface layers by air-water gas exchange and the St. Lawrence River, especially during periods of stratification. Vertical mixing in the colder months hastened the restoration of an equilibrium state; when fall overturn occurred, Lindane was mixed throughout the lake, and the water column was able to fully equilibrate with the atmosphere.
DYRESM-Ont currently only permits modelling of soluble gases such as Lindane. Numerical instabilities occurred for test simulations using insoluble chemicals, resulting from an over-saturation of the surface layer in Lake Ontario during any 15 minute time step, \( \Delta t \). The maximum gas transfer velocity \( K_{\text{tot}} \) was proposed to be \( K_{\text{tot}} \ll H_s/\Delta t \), where \( H_s \) is the height of the surface layer. Results from tests performed to evaluate the model's physical limits are presented in appendix D.
Chapter 4

Conclusions

The model DYRESM-Ont was created to predict vertical Lindane concentration distributions in Lake Ontario resulting from air-water gas exchange. Environmental modelling, and particularly the modelling of lake mixing processes, can be quite complex due to the large number of factors which must be taken into account. In this research, the influence of atmospheric conditions on concentration profiles in the lake was examined. Several conclusions were drawn from this investigation which relate to the model itself, the processes that affect Lindane concentration, and the effects of atmospheric changes on the concentration structure in the lake.

- DYRESM-Ont produced accurate and consistent predictions for up to four years when supplied with the meteorological data from the IFYGL 1972/1973 and measured atmospheric Lindane concentrations. However, to better determine the accuracy of the model, it would be preferable to have more year-round field measurements of Lindane at a variety of depths in Lake Ontario.

- The model is currently operational for air-side limited chemicals only. Less soluble compounds could be accommodated if the time step in DYRESM-Ont were decreased.

- A 50 day start-up period was required in all simulations for the lake to achieve chemical equilibrium with the atmosphere.

A number of conclusions concerning the nature of Lindane concentration and transport in Lake Ontario were formulated:

- Air-water gas transfer is the dominant process affecting Lindane concentrations in Lake Ontario. Flux through the surface of the lake was typically one to two
orders of magnitude greater than the daily mass entering the lake via the inflowing Niagara River or removed by the outflowing St. Lawrence River.

- The solubility of Lindane plays a large role in determining the concentration in Lake Ontario. Gas exchange of Lindane was predicted to be a net deposition into the lake during the late spring and early summer months, and a net volatilization out of the lake in the late summer and early fall. As the water in the lake warmed, Lindane's solubility decreased; concurrently, the air concentration decreased, and the direction of mass flux was into the atmosphere. When the lake cooled, the solubility increased, and the direction of gas flux was into Lake Ontario.

- An annual net deposition of approximately 50 kg was predicted to occur from air-water gas transfer of Lindane.

- Lake Ontario is near chemical equilibrium with the atmosphere. When the concentration of Lindane was altered, the lake came to equilibrium very quickly as a result of its high solubility.

The effects of atmospheric changes on Lindane concentration in the lake produced several interesting results:

- When atmospheric concentrations were altered, the lake attained equilibrium more rapidly when it was unstratified. During the period of stratification, some chemical mass could become trapped beneath the thermocline, but once fall turnover occurred, this chemical would be released and the lake would quickly reach an equilibrium state with the atmosphere.

- An increase in $C_a$ caused a proportional increase in $C_w$.

- Global climate change, as predicted by Global Circulation Models, would cause an increase in $C_w$. The most significant increases would occur from January through April, when the Lindane concentrations could increase by more than 0.2 ng L$^{-1}$ throughout the water column. Additionally, the period of stratification would be lengthened.

- Short-term injections of mass were rapidly dispersed by air-water gas exchange as the lake came to chemical equilibrium.

- The accuracy of the initial concentrations was unimportant. All simulations required a 50 day start-up period regardless of the environmental inputs or initial
conditions. The atmospheric Lindane concentration had a much greater impact than the initial inputs on the lake's concentration structure.
Chapter 4. Conclusions

Future Work

There are a number of ways in which this work could be continued or improved:

- More complete field measurements of Lindane would be useful in determining the validity of the current model’s predictions. Surface and deep water values should be taken several times each season to use for comparison.

- A reduction in the time step would permit modelling of mildly insoluble gases. For example, to model hexachlorobenzene, it would have to be reduced to less than one minute. This would increase the running time significantly and would probably require the use of a more powerful computer system.

- GASTRANS contains complete algorithms to determine certain properties of Lindane and carbon dioxide, as well as some algorithms for hexachlorobenzene. Ideally, subroutines for a variety of chemicals currently in use by the agricultural community could be added to the model, to determine the implications of the continuing use of organochlorine pesticides, some of which are on the Government of Canada’s Priority Substances List [11].

- For an inclusive model of concentration in lakes, all chemical pathways should be incorporated into the model, including half-life reactions, evaporation, sedimentary absorption and wet and dry deposition. Attempts to quantify these pathways for organochlorine pesticides have been made by Quémarais et al. [42], Mackay and Leinonen [30] and McConnell et al. [35]. Finally, if biologically reactive chemicals are of interest, the effects of biota must be included.
Appendix A

Analytical Solution for Diffusion Subroutines

The diffusion subroutines, FCT and DIFUSE, were tested to ensure proper operation. An analytical solution was prepared to compare results of the vertical downwards diffusion of heat and mass; the following example is for temperature only, however, the process is identical for concentration.

The initial temperature throughout the lake, \( T_i \), was set to 10\(^\circ\)C. At time \( t = 0 \), a step function was employed to elevate the surface temperature, \( T_s \), to a constant \( T_o = 20\)^\(\circ\)C (see figure A.1).

The lake was assumed to be a semi-infinite plane, i.e. deep enough to avoid a bottom boundary.

\( \theta \) was defined as

\[
\theta(z, t) = T(z, t) - T_i
\]

where \( T(z, t) \) is the temperature at point \( z \) and time \( t \), \( T_i \) is the initial temperature. and

\[
\begin{align*}
\text{t < 0} & \quad T_s = T_i = 10\,^\circ\text{C} & \quad T_w = T_i = 10\,^\circ\text{C} \\
\text{z} \\
\text{t \geq 0} & \quad T_s = T_o = 20\,^\circ\text{C} & \quad T_w = T(z, t) \\
\text{z}
\end{align*}
\]

Figure A.1: Conditions (i) initially and (ii) after implementation of step function.
$T_o$ is the imposed surface temperature, all in ($^\circ$C).

The following boundary conditions were established:

$$\theta(0, t) = T_o - T_i = 10^\circ C$$

$$\theta(z \to \infty) \to 0$$

An initial condition was set:

$$\theta(z, 0) = 0$$

The heat equation is defined as

$$\frac{\partial^2 \theta}{\partial z^2} = \frac{1}{\kappa \frac{\partial}{\partial t}}$$

(A.1)

where $\kappa$ is the thermal diffusivity in water ($m^2 s^{-1}$), $t$ is the time elapsed ($s$), and $z$ is the depth from the surface ($m$).

To determine a solution to the heat equation, the partial differential equation (PDE) of equation A.1 was transformed into an ordinary differential equation (ODE).

A new variable, $\xi$, was defined, such that

$$\xi = \frac{z}{\sqrt{4\kappa t}}$$

The PDE was converted from a function in $z$ and $t$ to a function in $\xi$.

$$\frac{\partial \theta}{\partial t} = \frac{\partial \theta}{\partial \xi} \cdot \frac{\partial \xi}{\partial t} = \frac{-\xi}{2t} \cdot \frac{\partial \theta}{\partial \xi}$$

$$\frac{\partial \theta}{\partial z} = \frac{\partial \theta}{\partial \xi} \cdot \frac{\partial \xi}{\partial z} = \frac{1}{\sqrt{4\kappa t}} \cdot \frac{\partial \theta}{\partial \xi}$$

$$\frac{\partial^2 \theta}{\partial z^2} = \frac{1}{\sqrt{4\kappa t}} \cdot \frac{\partial \theta}{\partial z} = \frac{1}{4\kappa t} \frac{\partial^2 \theta}{\partial \xi^2}$$

Substituting the new terms into the heat equation,

$$\frac{1}{4\kappa t} \frac{\partial^2 \theta}{\partial \xi^2} = \frac{-\xi}{2kt} \cdot \frac{\partial \theta}{\partial \xi}$$

an ODE in terms of $\xi$ only was obtained,

$$\frac{\partial^2 \theta}{\partial \xi^2} + 2\xi \frac{\partial \theta}{\partial \xi} = 0$$

(A.2)
with updated boundary conditions:

\[
\theta(\xi = 0) = T_o - T_i
\]
\[
\theta(\xi \to \infty) \to 0
\]

Equation A.2 was integrated once using an integration factor \( e^{\xi^2} \),

\[
\frac{\partial \theta}{\partial \xi} = ae^{\xi^2}
\]  

(A.3)

and a second integration produced:

\[
\theta(\xi) = a \int_0^\xi e^{-m^2} \, dm + b
\]  

(A.4)

where \( a \) and \( b \) are constants.

Using the error function,

\[
erf(\xi) = \frac{2}{\sqrt{\pi}} \int_0^\xi e^{-m^2} \, dm
\]  

(A.5)

with \( erf(\infty) = 1 \), \( erf(0) = 0 \), and \( erfc(\xi) = 1 - erf(\xi) \), the boundary conditions were implemented:

\[
\theta(\xi = 0) = 0 + b = T_o - T_i \quad \therefore b = T_o - T_i
\]
\[
\theta(\xi \to \infty) = a \sqrt{\frac{\pi}{2}} + b \to 0 \quad \therefore a = \frac{-2}{\sqrt{\pi}}(T_o - T_i)
\]

A solution to the ODE was found to be:

\[
\theta(\xi) = (T_o - T_i)(1 - erf(\xi))
\]

(A.6)

With substitutions for \( z, t, \theta \) and \( erfc \), the final solution was determined:

\[
T(z, t) = (T_o - T_i) erfc\left(\frac{z}{\sqrt{4\kappa t}}\right) + T_i
\]

(A.7)
Appendix B

Properties of Lindane

Lindane is a highly toxic organochlorine insecticide and fumigant which was widely used in agricultural applications, such as the treatment of greenhouse vegetables and Christmas trees, and is still in use in lotions, creams and shampoos for humans to control lice and mites [38]. It is the most abundant pesticide in the Great Lakes [43].

Lindane is a 99% pure isomer of Benzene Hexachloride (BHC), known as γ-hexachlorocyclohexane (γ-HCH or Cl₆C₆H₆). It has not been produced in the United States or Canada since 1977, although it is still imported and used in very limited quantities [39]. In the U.S., its use is heavily restricted by the Environmental Protection Agency (EPA).

Toxicity and Ecological Effects

Symptoms of acute exposure in humans can include mental and motor retardation, convulsions, respiratory failure, and skin infections. Lindane is expected to be a carcinogen, especially as a result of chronic exposure [39].

Lindane can be present in the air, or attached to small particles for up to 17 weeks, and may travel long distances. In soil, sediments and water, it is broken down by algae, fungi and bacteria to less harmful substances. Lindane is particularly persistent in fatty tissue of animals, and can remain in some vegetables for several months following application [38].

The EPA has set a limit of 0.2 ppb, or 200 ng L⁻¹ on drinking water [39]. In Ontario, the limit is 0.01 ppb [41].
Chemical Properties

Molecular formula: \( \text{C}_6\text{H}_6\text{Cl}_6 \)
Molecular weight: 290.8314 g \( \text{g mol}^{-1} \)

Diffusivities in air and water at \( T_a \sim 20^\circ \text{C} \):

\[
D_a \approx 5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}
\]
\[
D_w \approx 6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}
\]

Schmidt numbers in air and water at \( T_a \sim 20^\circ \text{C} \):

\[
Sc_a \approx 2.75
\]
\[
Sc_w \approx 2000
\]

Solubility at \( T_a \sim 20^\circ \text{C} \):

\[
\beta \approx 20000
\]

Half-life of Lindane in soil [38]:

\[
t_{1/2} = 1.2 \text{ years}
\]

Half-life of Lindane in water [38]:

\[
t_{1/2} \approx 300 \text{ days}
\]
Appendix C

Julian Day Conversion

The data provided by CCIW was given in terms of Julian days. The following table gives the conversions for both normal years and leap years; 1972 (of the IFGYL) was a leap year.

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</table>
Appendix D

Stability Limits in DYRESM-Ont

In theory, DYRESM-Ont is only operational for air-side limited gases, such as Lindane. As discussed in section 2.4, the model is likely to become numerically unstable if, during a single time step, a surface flux over-saturates the uppermost layer. Ideally, the model should be able to predict concentrations for gases of all solubilities.

Shown in figure D.1, air-side limited gases are those with the highest solubilities at the top of the graph. There is a narrow transition zone, below which various poorly soluble gases are marked. At 20°C, Lindane has a solubility $\beta > 10,000$ and a Schmidt number $Sc_w \approx 2000$ [13], which would place it near atrazine.

To determine the physical solubility limits of DYRESM-Ont, a lower solubility was imposed on Lindane. This was done by fixing the gas transfer velocity, $K_{tot}$, at various values to investigate the numerical stability limits. $K_{tot}$ is a function of many variables, including the Schmidt number $Sc_w$, the Bunsen solubility $\beta$ and environmental factors, so a simple reduction of $\beta$ was insufficient to determine the operational threshold of the model. No inputs or other variables were altered.

From the stability limits derived in section 2.4,

$$\Delta t \ll \frac{H_s}{K_{tot}}$$  \hspace{1cm} (D.1)

$$K_{tot} \ll \frac{H_s}{\Delta t}$$  \hspace{1cm} (D.2)

In DYRESM-Ont, the timestep $\Delta t$ is set at 15 minutes. The smallest possible depth of the surface layer is $H_{s,min} \approx V_{min}/A_s$, where $V_{min}$ is the minimum layer volume allowed by the model, and $A_s$ is the surface area:

$$V_{min} = \frac{V_{total, lake}}{150 \text{ layers}} \approx \frac{1705 \times 10^9 \text{ m}^3}{150}$$
Figure D.1: Schmidt number in water vs. solubility for various tracers. momentum, and heat for a temperature range (°C) as indicated; filled circles refer to a temperature 20°C. From Jähne and Haussecker [22].
A maximum for the gas transfer velocity can be approximated:

\[
A_s \approx 19000 \times 10^9 \text{ m}^2
\]

\[
\therefore \quad H_{s,\text{min}} \approx \frac{1705 \times 10^9}{(150)(19000 \times 10^9)} = 0.6 \text{ m}
\]  

(D.3)

A maximum for the gas transfer velocity can be approximated:

\[
K_{\text{tot}} \ll \frac{60 \text{ cm}}{0.25 \text{ h}} = 240 \text{ cm h}^{-1}
\]  

(D.4)

Some typical \( K_{\text{tot}} \) values for water-side limited substances include:

- Oxygen (O\(_2\)): \( K_{\text{tot}} = 0 - 2500 \text{ cm h}^{-1} \) (highly insoluble)
- Carbon Dioxide (CO\(_2\)): \( K_{\text{tot}} = 0 - 300 \text{ cm h}^{-1} \) (very insoluble)
- Hexachlorobenzene (HCB): \( K_{\text{tot}} = 0 - 40 \text{ cm h}^{-1} \) (mildly insoluble)

while \( K_{\text{tot}} \) for Lindane, which is very soluble, ranges from 0 to 1 cm h\(^{-1}\) [13].

The maximum limit approximated in equation D.4 indicates that the more soluble of the water-side limited gases might be acceptable for use with DYRESM-Ont. Several trials were performed to determine the maximum \( K_{\text{tot}} \) which could be used in the model without experiencing numerical instability at any point during a simulation. Neither CO\(_2\) nor HCB could be used successfully, even though HCB has a \( K_{\text{tot}} \) less than the suggested maximum, although not quite one order of magnitude less. The transfer velocity was set at a constant in several runs for a chemical with all the other properties of Lindane. The maximum allowable \( K_{\text{tot}} \) was found to be around 2.5 cm h\(^{-1}\), almost two orders of magnitude smaller than the limit from equation D.4. Instabilities occurred at all higher values. Thus, at present, DYRESM-Ont may only be applied to air-side limited gases.

The stability limit for \( K_{\text{tot}} \) can be expressed as a maximum time step, as shown in equation D.1. As suggested in section 2.4, over-saturation of the surface layer could be avoided if the time step were decreased to accommodate less soluble gases. Currently, \( \Delta t \) is set at 15 minutes, which is well within the proposed limits for Lindane by several orders of magnitude:

\[
\Delta t \ll \frac{H_{s,\text{min}}}{K_{\text{tot,\text{max}}}}
\]  

\[
\Delta t = 0.25 \text{ h} \ll \frac{60 \text{ cm}}{1 \text{ cm h}^{-1}} = 60 \text{ h}
\]  

(D.6)

but for CO\(_2\), with \( K_{\text{tot,\text{max}}} \approx 300 \text{ cm h}^{-1} \), \( \Delta t \ll 0.6 \text{ h} \), and for HCB, with \( K_{\text{tot,\text{max}}} \approx 40 \text{ cm h}^{-1} \), \( \Delta t \ll 2.4 \text{ h} \). For both chemicals, the current time step is no more than one order of magnitude below these limits.
For numerical stability, given the maximum $K_{tot} = 2.5 \, \text{cm} \, h^{-1}$ and the minimum $H_s = 60 \, \text{cm}$,

$$\Delta t \ll \frac{60 \, \text{cm}}{2.5 \, \text{cm} \, h^{-1}} = 24 \, h$$  \hspace{1cm} (D.7)

DYRESM-Ont’s present time step is about two orders of magnitude smaller than the limits specified here.

The model is restricted to simulations of air-side limited chemicals. To preserve numerical stability, a maximum value for $K_{tot}$ has been specified in DYRESM-Ont, and a threshold for the minimum time step was derived. Actual values must differ from the limits by at least two orders of magnitude to avoid instabilities. In order to change the time step to allow the study of water-side limited chemicals, a considerable number of alterations to the program would have to be made.
Appendix E

Code and Input Files: DYRESM-Ont

Included on diskette are the source code and input files for DYRESM-Ont.

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DYRESM-Ont is written in FORTRAN (PowerStation).
Bibliography


