The TRACING of a CONTAMINANT (TRITIUM) from CANDU SOURCES: LAKE ONTARIO

by

Karen June King

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Science

in

Earth Sciences

Waterloo, Ontario Canada. 1997

The TRACING of a CONTAMINANT (TRITIUM) from CANDU SOURCES: LAKE ONTARIO

Abstract

In any research program we begin with a hypothesis and when our expected results do not concur with the observed results we must try and understand the dynamics behind the changed process. In this study we were trying to understand the flux between regional groundwater systems, surface waters and sedimentation processes in order to predict the fate of contaminants entering one of the larger bodies of water in the world- Lake Ontario. This lake has increased levels of tritium due to anthropogenic inputs. Our first approach to the problem was to look at tritium fluxes within the system . Hydrological balances were constructed and a series of sediment cores were taken longitudinally and laterally across the lake.

The second approach was to quantify the sediment accumulation rate (SAR) within the depositional basins an d zones of erosion in order to improve the linkage between erosion control (sedimentation) and the water quality program.

In the last chapter the movement of tritium, by molecular diffusion, through the clayey-silts of Lake Ontario is quantified in terms of an effective diffusion coefficient. In these sediments effective diffusion equals molecular diffusion. In a laboratory experiment four cores of lake sediment were spiked with tritium . The resulting concentration gradient changes in the sediment porewaters after six weeks could be modeled by an analytical one-dimensional diffusive transport equation. Results calculated the average lab diffusion coefficient to be 2.7×10^{-5} $cm^{2\cdot}sec^{-1}$ which is twice that determined by Wang et al, 1952 but still reasonable.

Short cores (50 cm) from lake Ontario had observed tritium concentrations with depth that reflected a variable diffusive profile. The increases and decreases in tritium with depth could be correlated between cores. Monthly tritium emission data was obtained and correlations between peaks in the tritium profile and emissions were observed. Monthly variations in release emissions corresponded to approximately a one centimeter slice of core. An average calculated diffusion coefficient of theses cores was 1.0×10^{-5} $cm^{2\cdot}sec^{-1}$ which compares to Wang's coefficient of 1.39×10^{-5} $cm^{2\cdot}sec^{-1}$. This implies that tritium is moving through the sediment column at a rate equal to diffusion. The results were obtained for smoothed values. It was not possible to model the perturbations of the data with a one dimensional model. The dynamics of the system imply that tritium could be used as a biomonitor for reactor emissions, mixing time and current direction scenarios and that a better understanding of this process could be gained by future coring studies and a new hypothesis.

Acknowledgments

The author would first like to thank her children-Jeffrey, Julie and Christopher for putting up with mother typing on her computer, off to work and Waterloo. Their support is greatly acknowledged and they will be quite happy to see this completed.

I would also like to thank my friend Len for his support and encouragement to finish this thesis.

Shaun is responsible for my undertaking such a great adventure in the middle years of my life. I thank him for supporting me and trusting that I could do it-including the academics. I thank him for all the corrections, ideas and directions that permitted the completion of this thesis. I also thank him and his family for their kindness in lodging me during my visits.

My fellow researchers have also supported me through the years. Bob Drimmie, Jackie Morden-Murray and Ed Harvey were part of the Lake Ontario study.

I would like to thank Dr. Ed Sudicky for giving me a series of computer modelling codes to use with my data and for suggestions of which code would best fit my data. I would also like to thank Joel VanderKwaak for modifying the computer program FIN1FIT to DIFFIT and for his comments and suggestions during the research studies.

Dr. Ed Sudicky, Dr. Bob Gillham and Dr. Shaun Frape are to be thanked for reading through this longer than usual thesis and offering ideas and suggestions for improvement. Thank you also for attending and being a part of my committee.

My fellow co-worker Bert Risto helped me through the Lead-210 analyses and was always pushing me to get going. Lorna Chant spent time on the Limnos with me helping to collect the data. Wayne Workman was responsible for collecting and analyzing the river water samples, some air samples and the cruise samples along the north shore of Lake Ontario.

I would also like to thank AECL for giving me the leave of absence to complete the course part of the thesis. AECL has also been generous in donating time towards the completion of this document.

The dynamics of a system can often be reflected in the stability of the process.

TABLE OF CONTENTS

Page

CHAPTER 1
General Introduction

3.0 General Site Description

4.0 Methods

CHAPTER 2
Tritium in Lake Ontario: Mass Balance

3.0 Results

CHAPTER 3
The Sedimentation Process as Determined by ^{210}Pb

CHAPTER 4
Tritium Diffusion in Sediment Porewaters

List of Tables

List of Illustrations

CHAPTER 1 **PAGE**

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 1

General Introduction

1. The Great Lake System

The Great Lakes-St. Lawrence River system contains one-fifth of the world’s surface fresh water. This system directly impacts the people of eight states and two provinces. It is necessary to know how the level of contaminants are changing in this ecosystem. Wastes are discharged into the lake by air, surface runoff and groundwater influxes. What happens to these wastes once they enter the lake system? What pathways will the contaminants take? This thesis will investigate this last basin of water in the Great Lakes system- Lake Ontario

To study the changing water quality in Lake Ontario, several aspects should be addressed. The sources of contamination entering the lake by surface water runoff, industrial discharges, and groundwater flow should be looked at. The one variable that has not been quantified is groundwater. Studies have shown that both shallow and deep groundwater systems are connected to surface water systems such as lakes (McBride and Pfannkuch, 1975, Lee, 1977, Winter, 1978, Lee *et al*, 1980, Frape,1979, Frape and Patterson,1981, Seigel *et al*,1990, Frape,1991, Drimmie *et al*, 1992 and Sellinger, 1995).

Studies on the transport of major ions from deep source systems into the shallow Quaternary sediments of the area have been undertaken (Desaulnier *et al*., 1982, 1986,
1988, 1990). In all cases these land based studies have shown diffusive fluxes of ions such as chloride and sodium in association with an isotopically depleted light water $^{18}O/^{16}O$.

To date a few studies of Great Lakes sediments have dealt with interstitial water quality, age or source of the waters (Kramer, 1962, Kemp, 1969, Lerman and Weiler, 1970, O'Connor and Meuller, 1970, Thomas *et al*, 1972a & b, Weiler, 1973, Torgersen *et al*, 1977, Nriagu, 1981, Murdoch, 1983 and Sly, 1984). Hydrogeochemical investigations in
southern Ontario have found the presence of highly saline sedimentary formation fluids in the shallow groundwater (McNutt *et al*. 1987; Frape *et al*, 1989 and Seigel *et al*,1990). The University of Waterloo in 1990 discovered sites in the bottom of Lake Ontario where highly saline fluids appear to be entering lake bottom sediments (Drimmie,1992). These saline fluids appeared to be a mixture of sedimentary formation brines and shallow meteoric groundwaters. There are numerous implications associated with such fluid flow, particularly for domestic water supply. Sedimentary formation fluids are known to contain very high concentrations of trace metals and have a high dissolved major element load.

Heavy metals, organic contaminants, radionuclides and nutrients enter a water system and are eventually transported across a sediment-water interface. Diffusion, advection, and sedimentation rates and chemical interactions control the fate of the contaminant. Contaminants may be adsorbing or diffusing downwards into the sediments or may be desorbing, diffusing upwards into the overlying waters. Two recent thesis have studied these aspects of the Great Lakes. Murray-Morden, (1994) studied the trace element geochemistry of Lake Ontario sediments and porewaters and Harvey, (1995) evaluated and developed methods for hydrogeologic studies in deep lakes with specific applications in the Hamilton Harbour, Western Lake Ontario.

In another project, which used a mass balance approach, a link was established between the loading ($kg \cdot a^{-1}$) of specific chemicals and the resulting concentration of these chemicals in the water, sediments, and biota of Lake Ontario (MacKay *et al*, 1994). The three compartment mass balance model of MacKay, and the mass balance model developed in this thesis for tritium input into Lake Ontario, look at atmospheric inputs, the water column and the sediment layer and give an appreciation for the relative importance of various fate processes . Both were developed to guide regulatory efforts.

Accuracy in dating the input of environmental contaminants into our surface water lakes is fundamental in an attempt to understand possible changes over time. Recent developments in measuring man's impact on the global environment over the past 200 years may provide us with a better quantitative understanding of past conditions and an approach to predicting future impacts of man (Schell and Tobin,1993).

2. Project Overview

This thesis is a part of a research program conducted by the University of Waterloo to evaluate the input of contaminants into the surface waters of Lake Ontario and to relate this loading to the hydrogeochemical conditions in the underlying sedimentary strata.. The objective of the overall program was to assess the quantity, quality and source of groundwaters and the degree of interaction between regional groundwater systems and surface water systems within the lake. Other researchers in this program include 1) R. Drimmie (PhD, University of Waterloo) who is addressing the geochemical and isotopic indicators of the formation water brine movement into Lake Ontario and Lake Erie sediments, specifically ^{18}O , ^{2}H and ^{36}Cl, 2) J. Morden , (1994) who looked at the trace element geochemistry of the Lake Ontario sediments and porewaters, and 3) E. Harvey, 1995 who evaluated and developed methods to collect hydraulic and geochemical data in deep lake sediments in order to estimate the magnitude of groundwater recharge into Hamilton Harbour by proposing a conceptual model for groundwater flow in to the harbour basin.

2.1 Objectives

The objectives of this research were:

1. To evaluate and predict the transport of chloride and tritium contaminants, as found in sediment porewaters in the Lake Ontario bottom hydrologic system, using a mass balance approach, diffusion and advection processes.
2. To evaluate the transport and accumulation of contaminants within the sediment system by measuring ^{210}Pb profiles of the sediment which determine sediment ages and accumulation rates.

2.2 Assumptions

1. The mass balance approach to tritium in Lake Ontario indicates the reliability of the hydrological parameters.
2. Pb-210 analyses can quantify the dynamics of the sedimentation profile. Profiles can indicate where depositional and erosional processes are occurring. Sediments retain their character at the time of deposition but groundwaters can move upwards and downwards without interference.
3. No lateral advective mixing occurs in the top 300 cm (ie. advection along a sediment layer).
4. The tritium diffusive profile in the sediments is a result of emission input data.

2.3 Scope

This study examines three parts of the advection/dispersion equation needed for modelling the contamination within Lake Ontario. The hydrogeological component of Lake Ontario has been addressed by investigating tritium in the lake system. Estimates of tritium inputs were calculated using air and water emission data from the reactors on Lake Ontario (Ontario Hydro,1972-1993). Tritium lakewater samples were obtained from Lake Ontario during separate cruises aboard the CSS LIMNOS (a Canadian Scientific Ship) in the years 1990 to 1992. These concentrations established baseline values.

The sorption component of the equation has been addressed by examining ^{210}Pb in the sediments. The dating of the sediment core and the definition of the SAR (Sediment Accumulation Rate) allows a visualization of the deposition of a metal contaminant. This part of the thesis shows where contaminant deposition would have taken place and the amount of expected accumulation. This SAR number can then be used in conjunction with whole basin models and with another metal of known K_d.

The third part of this research examines the diffusion of tritium and chloride into Lake Ontario sediments. Sediment cores were taken in 1992 and 1993 within Lake Ontario in different depositional basins and laboratory column experiments were conducted. This project examined the downward diffusion of tritium and the upward diffusion/advection of chloride in site specific locations within the lake basin. The molecular diffusion coefficients were calculated using a 1-D advection-dispersion equation and a using nonlinear least-squares fitting analysis

3. General Site Description

3.1 Physiography-Surface Drainage

Lake Ontario is located at the eastern extent of the Great Lakes system and empties into the St. Lawrence River. It covers an area of 19,800 km^2, and is the center of a drainage basin that encompasses 70,000 km^2. The drainage basin stretches 450 km east to west, and 385 km north to south. The average water depth is 75 m, with a maximum water depth of 242 m. Lake Ontario is the third deepest lake in the chain of lakes (Haefeli, 1972).

3.2 Regional Geology of the Lake Ontario Basin

Lake Ontario is located in a large depression that was cut into early to mid-Palaeozoic limestones and shales by rivers and glaciers. The Lake is bounded to the northwest by the Algonquin Arch, to the south, by the Allegheny Plateau and to the east the PreCambrian Frontenac Axis and the Adirondack Mountains. A north-south cross-section through Lake Ontario and Lake Erie indicates that both lake basins have been eroded through the Palaeozoic shales and are now bounded by escarpments composed of more resistant carbonates and sandstones (Figure 1.1).

Figure 1.1: Geological cross-section of Lake Ontario and Lake Erie (from Hough, 1958).

Thomas *et al*. (1994) have reviewed the papers dealing with the tectonic stability of the lower Great Lake area. It is their hypothesis that the St. Lawrence rift system extends into the Great Lakes. In their paper they present evidence of faulting in modern sediments which lie on the bottom of Lake Ontario along the southern boundary of the extension of the rift into Lake Ontario, as proposed in the series of papers by Adams and Basham (1989). They also describe structures spatially related to both magnetic and topographic lineaments which may mark the northern side of the rift.

3.3 Quaternary Geology

During the Pleistocene (glacial) and Holocene (postglacial) times, a complex record of erosion and deposition developed in the Lake Ontario basin (Martini and Bowbly,1991). During glaciation, the continental ice sheets flowed from the north and northeast and when they reached the Great Lakes region were funnelled, thickened, and moved as lobes into the preexisting river valleys (Prest 1970; Gadd 1971; Muller and Prest 1985). The Great Lake system has been in existence since the retreat of the ice from the last glaciation (the Wiconsinian). At 12,000 B.P. it was called Lake Iroquois and following the diversion of Upper Great Lakes drainage to the Ottawa River at 10,500 B.P. there was a reduced water supply and levels dropped (Anderson and Lewis, 1985). At about 9,000 B.P. the Upper Lakes drainage returned and the waters have flowed from Lake Superior to the St. Lawrence River system.

3.4 Surficial Sediments

Thomas *et al*, (1972b), described in detail the surficial sediment distribution in Lake Ontario**.** (Figure 1.2). The inshore zone is defined by the distribution of glacial till, sands and bedrock. In some areas particularity between Hamilton, Toronto and east to Darlington, the tills have been removed, exposing bedrock. Figure 1.3 shows the location of the sediment cores taken for this study. The cores (DP series-off Darlington) were difficult to obtain and the few cores taken were sand. The tills overlie the bedrock base of the lake basin and dip inward from the lake periphery beneath the overlying glaciolacustrine clays. The sediment cores taken in other parts of the lake as shown on Figure 1.3 would be defined as glaciolacustrine clays.

Figure 1.2: Surficial sediment distribution in Lake Ontario.

3.5 Geomorphology and Sedimentation

Lake Ontario has been subdivided into three deep sedimentary basins, the Niagara, Mississauga, and Rochester basins, separated by bathometric sills, and a fourth shallow (less than 40 m deep) basin, the Kingston basin, situated at the eastern end of the lake (Figure 1.4 , Thomas *et al*, 1972a, 1972b). The deepest part of the Lake Ontario basin (depth about 242 m) is in the central portion of the Rochester Basin.

Figure 1.4: Bathymetry of Lake Ontario and major depositional zones.

The amount of information about modern sediments in the lake is large, and inventories of their ages, rates of sedimentation, and concentrations of many ions have been established (Thomas *et al*, 1972a, 1972b). Similarly the sources of the sediments and the processes of their dispersal are reasonably well known (Haras and Tsui 1976, Rukavina, 1976, and Martini and Kwong 1985).

3.6 Regional Hydrology-Basins

The interaction between deep regional flow systems and localized groundwater concentrations has been investigated by Frape *et al*, (1989 and 1991). Implications of upwards groundwater flow were summarized in Murray- Morden, 1994. In her geochemical analyses of pore waters in Lake Ontario cores she found three categories of cores. The first had elevated chloride concentrations and high concentration of trace elements and these cores were presumed to be affected by the input of deep groundwater input; the second set of cores showed little or no effect of groundwater input (no increased chloride or trace elements) and the third set of cores were a combination of the two. She includes in her thesis a table (Table 1.1) which best describes the processes influencing the distribution of trace elements in the sediments and porewaters.

TABLE 1.1

Processes Influencing the Distribution of Trace Elements in the Sediments and Porewaters

(Murray Morden,1994)

Processes	**Description**	**Evidence**
Formation Water Inputs	Movement of groundwater by advection into sediment system. Diffusion of solutes from formation water into sediments.	Increases in concentration with depth for chloride and trace elements in porewater.
Diagenesis	Interaction between the sediments and porewaters. Includes adsorption/desorption and precipitation/dissolution reactions, Eh, and pH equilibria.	Increases in concentrations of carbonate species with depth in cores, ie. Ca, Sr, and total carbon. Increases in SI with depth. $MnCO_3$ modelling results.
Anthropogenic Inputs	Includes atmospheric fallout, sewage and industrial effluent, spills, leaks, and any other effects of civilization on the natural environment.	Increases in concentrations of Zn and Pb in shallow samples in locations close to shore.

4.0 Methods

4.1 Water Sampling

Tritium samples were obtained from Lake Ontario during 1991 June and July on two separate cruises aboard the CSS LIMNOS (a Canadian Scientific Ship) (Figure 1.5). The first set of surface waters and depth profiles was obtained in a cooperative cruise with the University of Waterloo, and the second set of samples on a cruise with Environment Canada. Samples from Lake Erie were taken on a 1991 July cruise in cooperation with Environment Canada. Other tritium samples were obtained during 1991 July on a cruise along the north shore of Lake Ontario, from the Bay of Quinte to Toronto, about 1.6 km offshore. River discharge samples were taken on a road trip. Other tritium samples were taken 1992 and 1993 (Chant *et al*, 1994).

Figure 1.5: The SS Limnos.

4.2 Air Sampling

To assess the tritium concentration in air, 10 samples were taken on Lake Ontario during 1991. Two methods, active and passive sampling, were used (Wood & Workman, 1992). In the active method, an air sample was pumped through a desiccant column filled with anhydrous calcium sulphate (Figure 1.6**).** This method was used for point sampling of HTO-in-air over a period of one hour. The passive diffusion method used standard 20 mL scintillation vials with a vial lid modified to contain a stainless-steel insert with a defined diffusion orifice (Figure 1.6). The HTO vapour diffuses through the orifice and is trapped by tritium-free water inside the vial. Samplers can be left for periods up to one month. In this study, one set of samplers (four vials per set) was left exposed aboard the SS Limnos for 1.8 days, and the second set was left exposed for 1.4 days.

Figure 1.6: Monitoring of tritium in air.

4.3 Collection of Sediment Cores

Cores were taken along areas of magnetic anomalies as observed on aeromagnetic total field maps of Lake Ontario (Figure 1.3). They were taken using a gravity corer (Figure 1.7) (6.3 cm diameter tube), subsampled from a box core (Figure 1.8) or piston cored (alpine type)(Figure 1.9). Sample size varied according to core recovery and depth of core recovered ranged from 4 cm to 320 cm. The first two coring methods are useful for obtaining short cores (ie. less than one meter). The alpine corer is a 600 kg weight attached to steel tubing and is capable of coring to 60 feet using three twenty foot sections. The steel sections are lined with plexiglass tubes.

All cores were immediately cut into sections, capped, sealed, labelled and boxed. They were stored under refrigerator conditions of approximately 4°C both on the Limnos and back at the laboratory to minimize biological activity. Eight of the smaller (<1m) cores were sectioned immediately upon recovery using the procedure shown on Figure 1.10. They were sectioned in one centimeter slices to 10 cm, 2 cm to 20 cm and 5 cm slices to end.

The four cores that were used in the laboratory diffusion experiment were frozen. After the experiment, these cores were sliced by a jig saw and sediments and porewaters separated by centrifugation. The sediments were analyzed for ^{210}Pb and the porewaters for tritium..

Figure 1.7: Sediment sampling using a gravity corer.

Figure 1.8: Sediment subsampling in a box core.

Figure 1.9: Piston core: Alpine type.

Figure1.10: Sediment slicing techniques.

4.4 Laboratory Procedures

The porewaters were separated from the sediment by low speed centrifugation. The porewaters were analyzed for tritium and anion concentrations. Core sections were dried and moisture content was determined by drying at 60°C. The sediment was crushed and homogenized using a mortar and pestle before ^{210}Pb determinations.

4.4.1 Tritium Analyses

Tritium analysis of samples taken in the Great Lakes requires high-precision, ultra trace analytical facilities to measure the low-level radioactivity. All porewater samples were analysed at the Environmental Isotope Laboratory (EIL) at the University of Waterloo.

Currently, two low-level liquid scintillation counters (LSC) are used at Chalk River Laboratories (CRL): a Wallac Quantulus 1200 and a Packard 1550, both installed in a low-level facility. Both LSC's use optimized window settings for the lowest background and highest counting efficiency achievable with a standard polyethylene vial (Brown, 1989). Most of the samples were analyzed on the Quantulus 1200, which has an efficiency of 25 ± 0.2% and a detection limit of 1.4 $Bq{\cdot}L^{-1}$. The Packard has an efficiency of 21.6 ± 0.3% and a detection limit of about 2.2 $Bq{\cdot}L^{-1}$. For low-level samples, the counting time was about 400 minutes per sample. At the University of Waterloo (EIL), a Packard 1550 is used and it has an efficiency of 28.5% with a detection limit of 2.4 $Bq{\cdot}L^{-1}$.

CHAPTER 2

Tritium in Lake Ontario: Mass Balance

1. Introduction

Tritium is present in today's environment as a result of cosmogenic, atmospheric weapons testing and industrial nuclear sources (Brown, 1989). Tritium, with a half life of 12.3 years, readily enters the hydrologic and terrestrial systems and it has been useful as a tracer in hydrogeological investigations, atmospheric, surface water and ocean studies (Rozanski *et al*, 1991; Ostlund, 1984; Michel, 1976; Broecker *et al*, 1986). In the last 40 years, the major source of tritium to the atmosphere has been from weapon tests. As tritium levels return to pre-bomb values, the industrial emissions of tritium are becoming more important (Rozanski *et al.*, 1991).

The amount of tritium discharged from CANDU (CANada Deuterium Uranium, registered trademark) facilities into Lake Ontario was assessed using field data obtained in 1991 and 1992, and Ontario Hydro emission release concentrations. The average concentrations and the spatial and temporal heterogeneity’s of tritium in Lake Ontario were obtained by taking both surface and deep water samples. Samples of surface waters from Lake Erie and other rivers entering Lake Ontario were taken for background information and model input parameters. The effect of tritium release to the lake before volume dilution was analyzed by taking surface water samples along a transect from Darlington to Pickering. The tritium-in-air concentration gradient from the reactor release point to air over various locations on the lake was measured by taking samples of atmospheric moisture using active and passive methods of sampling. In this chapter, a mass-balance approach is used to evaluate the contribution of tritium from facilities to Lake Ontario.

2. Sources of Tritium

Tritium exists in the atmosphere primarily in the form of HTO, HT, and CH_3T. The latter two are oxidized slowly in the environment to HTO, which is removed from the atmosphere by precipitation and isotopic exchange with continental and oceanic surface waters.

2.1 Natural Tritium

The production rate of natural tritium is estimated to be 0.25 atoms·cm^2·s^{-1} (Craig & Lal, 1961). The global inventory of natural tritium is negligible (3.6 kg) compared with other inputs.

2.2 Bomb Tritium

Major releases of bomb tritium occurred in 1954, 1956, 1958 and 1961 (Michel, 1976). It was estimated that the total tritium produced by nuclear explosions was 550 ±160 kg, about 150 times the natural global inventory.

Bomb tritium has been almost completely removed from the atmosphere. Figure 1.1 shows the tritium concentration changes in precipitation at Ottawa and in the Ottawa River (Brown, 1989). Precipitation and Ottawa River values almost reached 1000 Bq·L^{-1}. This figure shows the decline in values to 1988. Tritium levels in precipitation have returned to close to pre-bomb values (less than 1.0 Bq·L^{-1}) except in mid-continental areas (Rozanski *et al*, 1991). The concentrations of tritium in precipitation measured at Ottawa, Canada, have declined from a high concentration of approximately 120 Bq·L^{-1} (1000 TU; 1 TU is one tritium atom per 10^{18} hydrogen atoms) in 1965/66 (Brown, 1989) to 4.4 Bq·L^{-1} (7 TU) in 1991. In the tropics, values between 0.36 and 0.72 Bq·L^{-1} (3 and 6 TU) are now commonly observed (Rozanski *et al*., 1991). Long-term trends of tritium concentration in monthly precipitation for several stations belonging to the IAEA/WMO network for isotopes in precipitation indicate that relatively high concentrations persist in the northern hemisphere. Until 1972, the tritium content in precipitation at Vienna and Ottawa had been similar (Rozanski *et al*., 1991). From 1980 onwards, Ottawa has had elevated tritium concentrations relative to Vienna. This could suggest a growing relative importance of input from other regional sources, such as CANDU reactors.

2.3 Tritium from Heavy-Water Reactors

Currently, total industrial releases correspond to ~25% of the global natural production of tritium in the atmosphere (Rozanski *et al*., 1991). Ontario Hydro currently operates 20 CANDU reactors , with a gross generating capacity of 14 000 $MW_{(e)}$. Twelve of the reactors are located on the north shore of Lake Ontario, eight at the Pickering Nuclear Generating Station (PNGS) and four at the Darlington Nuclear Generating Station (DNGS). The major source of tritium in a CANDU reactor is neutron activation of the heavy-water (D_2O) moderator and coolant. The concentration of HTO in the heavy water is a function of the reactor power level and the irradiation time. Tritium is released during routine operations via evaporation or exchange and during events when D_2O, containing HTO, leaks into effluent streams.

Emissions to the atmosphere and to the local waters from Ontario Hydro nuclear power stations, have not exceeded 1% of the specific site derived emission limits based on international standards. Routine environmental monitoring of air, precipitation, milk, drinking water, and fruits and vegetables in the vicinity of nuclear facilities is used to evaluate tritium concentrations (Ontario Hydro, 1992).

Table 2.1 shows the effluent and air emissions for the nuclear generating stations on Lake Ontario for the year 1991. Ontario Hydro (1992) reports that the total tritium emissions to water from PNGS are 12.5 x 10^{+5} $GBq \cdot a^{-1}$ and from DNGS 2.9 x 10^{+5} $GBq \cdot a^{-1}$.

TABLE 2.1

Tritium Emissions from Reactors.

	WATER	AIR
Lake Ontario		
PNGS*	4.4 E + 05	8.1E + 05
DNGS*	7.0E + 04	2.20E + 05
Oswego**	1.37E + 01	1.48E + 00
Total	5.1E + 05	10.3E + 05

*Annual Summary and Assessment of Environmental Radiological Data for 1991 Ontario Hydro, HSD-HP-92-9

** Power Research Reactors in Member States - 1972 Edition by the IAEA, 1972.

3. Results

3.1 Lake Erie

To assess the input parameter for the tritium model, water samples were collected from Lake Erie. Twelve samples were taken in June and five in September 1991. Their average tritium concentration (Table 2.2) was 6.6 ± 0.6 $\mathrm{Bq{\cdot}L^{-1}}$ (54 TU). The Niagara River, which flows into Lake Ontario, had an average concentration of 6.9 ± 0.7 $\mathrm{Bq{\cdot}L^{-1}}$.

TABLE 2.2

Lake Erie Tritium - 1991.

	TU	+/- TU	Bq/L	+/- Bq/L
June	68	7	8.15	0.84
	65	3	7.79	0.36
	56	3	6.71	0.36
	52	4	6.24	0.48
	43	6	5.16	0.72
	48	5	5.76	0.60
	58	4	6.95	0.48
	62	4	7.43	0.48
	61	4	7.31	0.48
	57	4	6.83	0.48
	46	3	5.52	0.36
	49	5	5.88	0.60
September	53	6	6.35	0.72
	55	6	6.59	0.72
	52	6	6.24	0.72
	52	6	6.24	0.72
	56	6	6.71	0.72
AVERAGE	54.9	5	6.58	0.60

3.2 Lake Ontario

Nine rivers that flow into Lake Ontario were analyzed for their tritium concentration (Table 2.3). Tritium concentrations were higher in river samples closer to PNGS. This suggests that air emissions of HTO are transferred from the atmosphere to local catchment areas which subsequently feed the rivers that flow into the lake. It should be kept in mind that there would also be seasonal variation of tritium in these rivers. In the spring time when groundwater runoff would be high, tritium values will change.

Figure 2.2 shows the two transects made on Lake Ontario in 1991 June and July. Fifty samples were analyzed, and had an average tritium concentration of 9.0 +/- 0.8 $Bq \cdot L^{-1}$ (75 TU). Figure 2.3a shows the variation of Lake Ontario surface waters on a west-to-east transect for 1991 June data (10 samples).

TABLE 2.3

River Inputs to Lake Ontario 1991

Location	**Distance from PNGS (km)**	**Concentration (Bq/L)**
Rouge River	0	11.5 +/-0.3
West Dufferin Creek	8	7.0 +/-0.4
Oshawa Creek	18	8.9 +/-0.4
Wilmot Creek	45	5.5 +/-0.3
Ganaraska River	70	4.9 +/-0.6
Trent River	125	5.8 +/-0.2
Salmon River	175	4.4 +/-0.2
Oswego River: SE Lake Ont.	230	8.8 +/-0.3
Lake Erie Inputs		
Niagara River	75	6.9 +/-0.7
Welland Canal	80	6.7 +/-0.7

Average value of river inputs (except Oswego)	6.8

Figure 2.3b shows the variability of the 1991 July sample concentrations, as shown in chronological order of sampling station. Station 21, located north of the mouth of Niagara Falls, was the first sample station and sample 79 was taken at the east end of the lake as shown on transect on Figure 2.2. Duplicate samples were taken at 7 stations.

Variations in tritium concentration with depth were tested using the results of lake-water profiles at two mid-lake stations: Stn W6 (Wilson) was sampled to a depth of 150 m, and Stn 08 (Rochester Basin) to a depth of 240 m (Figure 2.2 for locations). At both these stations, HTO concentrations average 8.7 ± 1.0 Bq$\cdot$L^{-1} and there was no apparent trend with depth (Figure 2.4). Lake water appears to be well mixed during these time periods, as indicated by the tritium concentrations and temperature profiles taken at the same time as sampling. These graphs could be interpreted as tritium layers through the water column. Stn 08 has two depths (125 m and 215 m) where concentrations change by almost 2 bequerels over 75 m. W6 shows two increases at 50 m and 125 m.

Water samples taken along a transect of the north shore of Lake Ontario were collected to determine near-shore, surface water, tritium concentrations. This 48 km transect, about 1.6 km offshore, should be indicative of near-shore tritium concentrations before dilution into the pelagic zone. The results show an increase in tritium from 8 to 32 Bq$\cdot$L^{-1} , or 67 to 267 TU, as one approaches Pickering NGS. The average of 19 samples was 14.4 +/- 0.6 Bq$\cdot$L^{-1} (120 TU) (Figure 2.5).

3.3 Air Sampling

The average HTO concentration of the ten air samples taken in 1991 July over Lake Ontario was 0.73 ± .015 Bq$\cdot$m^{3}. The average specific activity was 492 TU. This activity level is about 7 times higher than the specific activity of 75 TU in the lake water. The variation in activity is shown in Figure 2.6 and is plotted as distance from Pickering. The highest level of tritium was 2.95 Bq$\cdot$m^{3} at a location 40 km from Pickering, with the lowest activity 0.22 Bq$\cdot$m^{3} measured at the very east end of the lake (250 km distance).

The passive sampling method gave an average concentration of 1.85 ± 1.0 Bq$^{\cdot}$m^{3} . This is about 2 times that obtained by air pumping; but not significantly different. Passive samplers were left for one to two days on the ship while it cruised, while the pumped air samples were taken over an hour; therefore exact agreement was not expected.

Air samples taken in June 1991, 19 km southeast of DNGS, had concentrations of 96 Bq$^{\cdot}$m^{3} to 112 Bq$^{\cdot}$m^{3}, which were 30 times higher than the highest air sample collected 2 km from the station site on a cruise in July 1991. The wind was blowing directly from DNGS to the sampling site in June 1991. Measurements made using active sampling by air pumping are very sensitive to local conditions and may not reflect longer term averages.

3.4 Tritium in Lake Ontario: Mass Balance

To assess how much tritium Ontario Hydro's reactors release to the Great Lakes, the collected field data and Ontario Hydro data with other references and have been put together for a mass-balance approach. The assumptions used to calculate inputs of tritium included lake-specific input data such as lake area, volume, water flow rates, precipitation, and evaporation. The concentration of tritium in the lake is assumed to be the average calculated in 1991 (9.0 +/- 0.8 Bq$^{\cdot}$L^{-1}). Because Ontario Hydro currently has reactors located on the shores of the Great Lakes, it is reasonable to assume that other reactors could be built along the shoreline; it is of interest, therefore, to calculate how much the reactors contribute to tritium levels in Lake Ontario and suggest future trends in the levels.

The calculated components of the tritium-balance model is shown on Table 2.4, and it can also be seen in pictorial view on Figure 2.7.

TABLE 2.4

Tritium Balance in Lake Ontario

INPUTS	TBq	%	OUTPUTS	TBq	%
CANDU-water[1]	514	17	Lake Ont. outflow[7]	2040	67
CANDU-air to water[2]	620	21	Radioactive Decay[8]	810	27
BWR-Scriba[3]	15	1	Evaporation[9]	110	4
Lake Erie inflows [4]	1330	45	Sediment Diffusion[10]	68	2
Precipitation[5]	56	2			
Drainage[6]	426	14			
Totals	2960	100		3028	100

1. Ontario Hydro, 1992
2. Ontario Hydro, 1992, Assumed 60% of air-borne releases exchanged with the surface lake water
3. Gustafson (1970) BWR produce one order of magnitude less tritium. Assumed 40% air-water exchange based on opposite wind directions to PNGS.
4. Average Lake Erie tritium-6.7 $Bq \cdot L^{-1}$; outflow is 2.04×10^{11} $m^3 \cdot a^{-1}$
5. 1992 precipitation concentration of 3 $Bq \cdot L^{-1}$, area of lake(1.9×10^{10} m^2) and amount of annual precipitation (0.89m-reported by Mackay,1994)
6. Drainage for north side= area of north side of lake (3.0×10^{10} m^2) times average river concentration (6.8×10^3 $Bq \cdot m^3$) times precipitation (0.89m)= 184 TBq; Drainage for

south side= area (4 x 10^{10}m^2) times river avg, concentration 6.8 x 10^3Bq·m^3) times precipitation (0.89m) =242 TBq; Total Drainage= 426 TBq.
7. Average of 50 samples collected in 1991 (9.0 Bq·L^{-1}); outflow volume is 2.28 x 10^{11}m^3·a^{-1}.
8. Concentration in lake (9.0 Bq·L^{-1}) times volume (1.64 x 10^{12}m^3) times decay constant (0.056 a^{-1}).
9. O'Connor & Mueller, (1970) reported 66 cm·a^{-1} times area (19,800 km^2) times concentration (9.0 Bq·L^{-1})
10. Rate of diffusion calculated to be 40 cm·a^{-1} (Chapter 3,) times concentration (9.0 Bq·L^{-1}) times area of lake (19,800 km^2)

The mass balance shows that the calculated error between outputs and inputs is within 1% . It should be emphasized that many of these parameters are subject to variation and uncertainty and the actual error would be expected to be closer to 10% would not be unreasonable because of the many assumptions made in the data. However a calculated error of 1% is encouraging in that the hydrologic and meteorlogic parameters and data obtained must be reasonable. This mass balance was designed to give an estimate of the processes involved in tritium transfer. This mass balance is consistent with a model presented by O'Connor & Meuller (1970) for chloride in all the Great Lakes; their hydrological balance of Lake Ontario and the balance reported here are in agreement within a few percent indicating a reasonable input of hydrological variables.

The tritium contribution from the reactors is equivalent to the input from Lake Erie. If we assume that the input tritium levels from Lake Erie would represent the tritium concentration in Lake Ontario if no reactors were present, then Lake Ontario would have a tritium value close to 6.7 Bq·L^{-1} (56 TU). The current value is, however, 9.0 Bq·L^{-1} (75 TU) which is 2.3 Bq·L^{-1} (19 TU) above the Lake Erie value. Pickering Nuclear Generating Station started up in 1972 and has been operating for 19 years to 1991 while

Darlington has been operating since 1988. This increased value of 2.3 Bq·L^{-1} (19 TU) over 19 years of Pickering time (Darlington input to the lake is only about 10% of Pickering), translates into an increase of 0.12 Bq·L^{-1} (1 TU) per year. If we look ahead to 2000 AD, it could be expected that Lake Ontario levels could be 10.08 Bq·L^{-1} (84 TU) on the basis of the assumption that the inputs would remain constant.

Sixteen Lake Ontario water samples were taken in 1992 July to evaluate the changes in the ambient lake water concentration after one year. If there were only small changes we would see a change that would only be small and probably not significant. The average tritium concentration in the central area of the lake was 9.4 ± 0.8 Bq.L^{-1} (Table 2.5). This is not significantly different than the average 1991 concentration of 9.0 ± 0.8 Bq.L^{-1} but it was slightly higher. Four samples were also taken near PNGS along the north shore, and they averaged 17.0 ± 1.0 Bq.L^{-1}, slightly higher than the 1991 concentration of 14.4 ± 0.6 Bq.L^{-1}. These numbers indicate that the small ambient increase predicted from the reactors could be a reasonable assumption barring any major releases but this conclusion is questionable due to the increase being within the error margin of 10%.

There was an accidental release of tritium to the lake in 1992 (Chant *et al*, 1994) and this resulted in approximately 2.02 PBq of tritium being released to the water from PNGS. This release occurred one week after our 1992 sampling cruise. On August 25 and 26 another set of lake samples was taken from Port Hope, Ontario to Point Breeze, USA. In 1993 surface water samples were taken at ten locations (Chant *et al*, 1994). Results for the average tritium concentrations at mid-lake for the two sampling times show an increase of 1.68 Bq·L^{-1} for August and 2.64 Bq·L^{-1} in May 1993 over the base lake concentration of 9.4 Bq·L^{-1} taken in July 1992 before the accident. If the 1992 August release of an additional 2.02 PBq was mixed into the entire volume of the lake, the increase in HTO concentration predicted is 1.23 Bq·L^{-1} (10.3 TU). These values provide an independent estimate of the quantity of tritium released on August 2 and are consistent with the reported release value of 2.02 Pbq. These results clearly show that the impact of accidental release was very small.

TABLE 2.5

Lake Ontario water samples: 1992

Station	TU	+/- TU	$Bq \cdot L^{-1}$	+/- $Bq \cdot L^{-1}$
Stn 21	121	12	15.0	1.0
Stn 590	59	11	7.0	1.0
Stn 405	78	10	9.0	1.0
Stn 404	70	9	8.0	1.0
Stn 464	57	10	7.0	1.0
Stn 45	79	12	10.0	1.0
Stn 825	64	11	8.0	1.0
Stn 60	75	10	9.0	1.0
Stn 71	78	4	9.0	0.0
Stn 401	76	6	9.0	1.0
Stn 2	121	5	14.0	1.0
Stn 403	79	6	9.0	1.0
Stn 403-30 m	80	4	10.0	0.0
Stn 403-50 m	80	4	10.0	0.0
Stn 403-100 m	6	5	8.0	1.0
Stn 403-150 m	75	5	9.0	1.0
Average	79	8	9.4	0.8
Darlington-Pickering				
DP-1	82	5	10.0	1.0
DP-4	125	7	15.0	1.0
DP-8	214	11	26.0	1.0
DP-9	143	6	17.0	1.0
Average	141	7	17.0	1.0

4. Discussion

The mass-balance approach to tritium in Lake Ontario shows that CANDU reactors contribute 38% of the tritium input to the lake. With the background world tritium precipitation value being less than 1.0 $Bq \cdot L^{-1}$, we can assume that the tritium input from precipitation and drainage would also include contributions from the reactors. Precipitation values at the PNGS site are 100 times above the average used for the lake; we can assume the values for input shown in Table 4 are conservative. If we assume that precipitation and drainage are also largely a result of the reactor inputs over time, then the reactors contribute an amount of tritium to the lake, which is equal to that of inputs from Lake Erie.

The mass of tritium added to the lake each year by Ontario Hydro's PNGS and DNGS reactors is about 8% of the inventory of tritium currently in the lake. This number is generated by taking the total input from CANDU reactors(1134 TBq- Table 2.4) and dividing it by the total tritium in the lake (14,700 TBq). The mass of tritium added to the lake should also reflect the tritium in the precipitation and drainage. The reactors are adding a mass of ~1500/14700 or closer to 16% of the total inventory.

The whole lake average over time shows little input from the reactors' releases after volume dilution. The difference in lake concentrations between Lakes Erie (6.6 Bq·L^{-1}) and Ontario (9.0 Bq·L^{-1}) over 20 years can be used to estimate the change in HTO concentration caused by CANDU reactor inputs into Lake Ontario. This change is 0.12 Bq.L^{-1} (1 TU) increase per annum.. It should be noted that the level of tritium in the lake at the time of PNGS startup in 1971 was 14.8 Bq·L^{-1} (123 TU) (Lickly *et al*, 1983). The Bruce Nuclear Generating Station on Lake Huron is also discharging tritium to the Great Lakes system, so for the total CANDU input, there would have to be an assessment of this input. Radioactive decay has played a significant role in decreasing the tritium in the lakes that was present because of the bomb pulse in the mid 1960's (20.0 Bq·L^{-1}). More than thirty years and almost three half lives have lowered the tritium level to below lake concentrations since 1971 (when PNGS started up). This concentration of 9.0 Bq·L^{-1} in the lake is 700 times lower than the interim drinking water quality guideline proposed of 7,000 Bq·L^{-1} (previous level was 40,000) and should continue to be within the guidelines unless current discussions substantially lower the limit. This objective is interim until the

Canadian Drinking Water Guidelines (Health and Welfare Canada, 1989) for radionuclides are revised through a federal-provincial process. It is likely that technology advances will further decrease the amounts of tritium discharged to the environment.

Studies of the current regime in Lake Ontario have shown evidence of a coastal zone in which currents are predominantly parallel to the shore (Csanady, 1970). Concentrations of tritium that were measured along the north shore between PNGS and DNGS were 40% higher than the whole lake average value. These measurements indicate that the dispersion of reactor tritium and volume dilution are slower along the shoreline. These results can be confirmed by the shoreline model simulations of Klukas & Moltyaner (1996). They used the unplanned release of tritium from PNGS that occurred in 1992 August to study the dilution and dispersion of shoreline tritium and their model simulations were able to confirm the shoreline elevated tritium concentrations at the Ajax, Horgan, and Harris water supply plants within a factor of two.

Future predictions (year 2000) of tritium concentrations to Lake Ontario were made by Gorman & Wong (1978). They predicted that the tritium concentration would be 55 $Bq{\cdot}L^{-1}$. At the time of their prediction, the PNGS units were under construction and DNGS was still in the design phase. This thesis benefits from 15 years of measured reactor emissions and base data. Figure 2.8 shows the reactor-derived tritium input to Lake Ontario. There was a varied but increased reactor input until 1988 and the subsequent decrease reflects improvements in HTO emission controls implemented in the CANDU reactors. The large increase in 1992 is the result of an accidental release. On the basis of this model of tritium balance for Lake Ontario and on the assumption that there will be no other accidental large increases, we believe that the HTO concentration in Lake Ontario should not exceed concentrations measured following the nuclear bomb testing (20 $Bq{\cdot}L^{-1}$) (Lickly *et al*, 1983).

5. Conclusions

Tritium measurements collected from Lake Ontario during the summers, showed no discernible trends either spatially or with depth in all study areas except along the north shore. This helps to substantiate the assumption that the lake is uniform with respect to tritium; the mass-balance approach to tritium in Lake Ontario shows that Ontario Hydro is adding 48% of the annual input of tritium to Lake Ontario, which is about 8% of the inventory within the lake.

The inputs from reactor emissions have increased the tritium level in Lake Ontario (average 9.0 Bq.L^{-1}) over Lake Erie (average 6.6 Bq.L^{-1}) by 0.12 Bq.L^{-1}.a^{-1} or 2.28 Bq.L^{-1} since reactor startup in 1972. This is an increase of 36% over Lake Erie's tritium concentration and an increase of about 1 to 2% per year.

The average specific activity of air samples taken over Lake Ontario was 492 TU. This activity level is approximately 7 times higher than the average specific activity of 75 TU in the lake. This suggests that the tritium-in-air transfer exchange to lake water is important. Looking at the calculated input from reactor emissions shows that the air-to-water exchange is slightly higher than the input from the aqueous outlet. This tritium concentration in Lake Ontario is well within the new proposed interim drinking water quality guideline proposed (7,000 Bq·L^{-1}). To date, accidental releases of tritium to the lake have not increased the concentration substantially (Chant *et al*, 1994).

CHAPTER 3

The Sedimentation Process as Determined by ^{210}Pb

1. Introduction

The Great Lakes receive inputs of toxic metals and organic compounds from sources within and outside their watershed . Governments are moving towards a goal to regulate, educate and improve pollution strategies with the water quality problems associated with erosion, sedimentation and the delivery of nutrients and toxic contaminants to the Great Lakes. Lead-210 dating is a powerful tool for estimating sediment accumulation rates and provides a temporal framework in which to evaluate the environmental history of a lake and its catchment. ^{210}Pb dating allows the determination of the depth to which the contaminant could be found and ^{210}Pb results give the researchers an indication of the reliability of their results especially in the first few cm. It indicates for the purpose of this thesis, the reliabilty of the porewater tritium data.

Trace contaminants discharged into fresh-water sediments are subject to internal fluxes, external loading and hydrologic flushing. Trace metal contamination into the Lake has been recently described by Murray-Morden, (1994). Of the three major processes that influence the distribution of contaminants within a flow system, the third-anthropogenic inputs can be described by using lead-210 dating.

Its short residence time of ^{210}Pb in the lake water column was been observed by Flegal *et al*, 1989 . It was found that the isotopic composition of lead in the surface waters of Lake Ontario was very similar to that of lead in the atmosphere. At the pH of the lakes (8.0), the lead is hydrolyzed and/or scavenged by both biogenic and inorganic particles. The rate of removal is then dependent on the water depth and settling velocity. Because of this rapid turnover rate lead can be used as a tracer of atmospheric deposition and can therefore be a useful dating tool.

This radionuclide is distributed widely on the earth . Radium (^{226}Ra -half life of 1622 years) in the ground decays to radon (^{222}Rn-half life 3.8 days) which goes into the atmosphere and decays to ^{210}Pb (22.3 year half life) which is then deposited with particulates (Figure 1). Thus, in any sediment or bog sample, the total ^{210} Pb measured has a supported fraction from the radium present and an unsupported fraction; the unsupported fraction is used in the determination of time (Schell and Tobin, 1993). A good review of the information on ^{210}Pb global cycle and tracing applications is found in El-Daoushy, (1988). Since the 22.3 year half-life of ^{210}Pb is ideal for the time period since the industrial revolution, much attention is being given to the accuracy of the dates that can be determined from its measurement in core profiles. ^{210}Pb can be used to date sediments up to 250 years. Several models have been devised to interpret the data and the accuracy of these models provides considerable discussion amongst proponents of each one.

When collecting cores for ^{210}Pb dating, the questions of where to core, how many cores are needed, and how the results can be extrapolated to adjacent areas are essential for proper interpretations. The mud depositional boundary theory (MDB) theory was presented by Rowan et al. (1992) and the test data include this Lake Ontario data set (Rowan *et al*, 1995). It examined the variability in sediment accumulation rates within the depositional zone and showed that the number of cores taken for this study within Lake Ontario, was sufficient to obtain a representative sediment accumulation rate (SAR).

2.0 Methods

2.1 Sampling

Sediment cores were taken as described in chapter one and locations can be seen on Figure 1.3.

2.2 Laboratory ^{210}Pb Procedures

The concentration of ^{210}Pb is determined assuming secular equilibrium between ^{210}Pb and its daughter ^{210}Po. About 0.5 grams of the dried sediment sample is placed within a 45 mL teflon cup, the ^{209}Po is added along with a HCl/HNO_3 mix. To obtain acceptable recoveries of the ^{209}Po yield tracer (mean recovery 75%), the sample with the Po was digested using a microwave enhanced acid dissolution. Teflon cups were placed within a Parr bomb (Risto & Cornett, personal communication). The residue was then leached in 1.5N nitric acid. Following removal of the nitric acid by evaporation, ^{210}Po was electroplated on silver discs in a 1.5N solution of HCl over a period of 16 to 24 hours. The extraction and plating technique of Eakins and Morrison (1978), was modified slightly (Cornett *et al*, 1984). The activity of ^{210}Po was measured using alpha spectrometry. The discs were counted using alpha surface barrier detectors, and the counts accumulated in a multichannel analyzer.

Three procedures were used to determine the accuracy and precision of the ^{210}Po analyses (Cornett *et al*, 1992). A radiochemical yield tracer (^{209}Po) traceable to NBS 4327, confirmed the yield tracer activity against $^{210}Pb/^{210}Po$ solutions from Amersham Nuclear, and other laboratories. Secondly, the activity of a sample (CANMET, Energy Mines and Resources SRM DL-1A) was measured and the results agree with the expected value. Blanks were analyzed and showed no detectable activity above counter background. The background of the counting system was monitored at approximately bi-weekly intervals and was found to be <1% in all but the lowest activity samples.

2.3 Dating Cores

Accuracy in dating the input of environmental contaminants into our surface water lakes is fundamental in an attempt to understand possible changes over time. Recent developments in measuring man's impact on the global environment over the past 200 years may provide us with a better quantitative understanding of past conditions and an approach to predicting future impacts of man (Schell and Tobin, 1993).

Establishment of a sedimentary chronology is central to the task of developing historical records of marine and lacustrine heavy metal contamination and modelling diagenetic processes (Robbins and Herche, 1993). Goldberg,(1969) introduced ^{210}Pb dating thirty years ago. The introduction of the method of dating lake sediments by Krishnaswami et al,(1971) revolutionised the use of lake sediment records in studies of recent environmental change. There are 2000 published papers which have dealt with ^{210}Pb in sediments (Robbins and Herche, 1993). The sediment accumulation rate(SAR) and core dating is based on ^{210}Pb radiochronology (Robbins, 1978, Appleby and Oldfield, 1978, and Oldfield and Appleby, 1984).

There are two models which calculate the SAR from ^{210}Pb data. The first is the Constant Initial Concentration model (CIC) which assumes that the supply of ^{210}Pb is governed by the sedimentation rate and thus will increase or decrease in response to changes in sediment flux. Under these circumstances there is a monotonic decline in unsupported (atmospherically derived) ^{210}Pb in the sediments which is attributable to the radioactive decay of ^{210}Pb only. The total residual unsupported ^{210}Pb across a lake basin would vary proportionately with sediment accumulation rates (Oldfield and Appleby, 1984). The other model, the Constant Rate of Supply model(CRS) (Appleby and Oldfield,1978, Schell and Tobin, 1993, Binford et al, 1993) and it assumes that the supply of unsupported ^{210}Pb to the sediments is governed by the atmospheric flux of ^{210}Pb and is therefore independent of sedimentation rate. One would then expect non-monotonic ^{210}Pb profiles in sediments to result in response to changes in the sedimentation rate since increases in the sediment flux would dilute ^{210}Pb in the sediments (Blais et al, 1994). Blais et al, 1994 demonstrated that the discrepancies between CRS and CIC dates occur in cores where SAR has increased most dramatically in recent years; and CRS dates are consistently older than CIC dates. For Lake Ontario cores, sedimentation rates have not changed dramatically and calculations using the CRS model on two data sets illustrated little changes. ^{210}Pb dating will indicate the degree of mixing in the top sediment layer and sediment accumulation In general, heavy-metal pollution of sediments was apparent as early as the 1800's, becoming more prominent in the early 1900's and showed a very sharp increase between 1940 and 1970.

3.0 Results

3.1 Pb-210 Dating and Sediment Accumulation

Figure 3.2 shows specifically the location of the cores for which ^{210}Pb profiles were completed. Cores were taken longitudinally and vertically through the lake. The bathometric contours show the depth of water.

Figure 3.2: Location of sediment cores and bathometric details.

The decay corrected concentrations of ^{210}Pb for the twelve cores shown in the previous figure are plotted in Figures 3.3 to 3.7.

The profiles showing fluctuations in the ^{210}Pb exhibit a subsurface maximum and rapidly decrease. The ^{210}Pb profiles from the cores taken on the north shore could not be interpreted because no deposition of ^{210}Pb was taking place. These cores are sandy and there straight line results indicate non-deposition. Figures 3.4 and 3.5 show cores from two basins with different sedimentation rates. The ^{210}Pb concentration profiles usually follow classic log-linear depth profiles (Robbins, 1978). In the top few cm of the core PC 32 (Figure 3.6), the ^{210}Pb concentrations changed very little with depth and suggest that the accumulation of ^{210}Pb and sedimentation has been continuous. Figure 3.7 is indicative of a mixed layer in the top few cm, probably caused by biological activity within the top of the sediments (Robbins, 1978; Robbins *et al*, 1977).

The ^{210}Pb profiles were interpreted using the CIC mixing model (Model 3) of Robbins (1978). This model uses the advection-diffusion equation to describe the depth(Z) distribution of ^{210}Pb under the assumptions that the depth distribution is at steady state and is described by:

$$\delta C_s/dt = \delta(E_b \delta C_s/\delta Z)\delta\, Z - w\delta C_s/\delta - \lambda C_s$$

Using model 3, the equation can be solved and the change in C, can be described by a set of six parameters that are constant with time and only the mixing coefficient changes with depth. The parameters are: the rate of sediment accumulation (w, $\mathrm{cm \cdot a^{-1}}$), the activity of ^{210}Pb in settling particles (C_s $\mathrm{Bq \cdot g^{-1}}$), the background activity of ^{210}Pb supported by ^{226}Ra (C_o, $\mathrm{Bq \cdot g^{-1}}$), the depth of the surficial mixed layer (Z, cm), the mixing coefficient in the mixed layer (E_b, $\mathrm{cm^2 \cdot a^{-1}}$) and the radioactive decay constant (λ,$\mathrm{a^{-1}}$). Since changes in porosity are not existent except in core PC4, these small changes will have only a small impact on the calculation of the core chronology (Robbins,1978).

Table 3.1 shows the SAR results for the cores analyzed and include, the depth of water above the sediment, and the mixed layer thickness. The dates and SAR numbers for each section as determined by the SRC model have been incorporated into Figures 4 through 8 where appropriate. The raw data used in the calculations are included in the appendix as well as the other cores not shown above.

TABLE 3.1

Sediment Core Data

Core	**Mixed Layer**	**Depth of Water**	**Water Content**	**SAR**	**Mud DBD Theory**

	(cm)	**(m)**		**$g\cdot m^{-2}a^{-1}$**	
D2	0.0	80.0	0.170	88	Eros/Trans
DP3	0.0	45.0	.0319	202	Eros/Trans
DP4	0.0	50.0	0.321	195	Eros/Trans
PC31	5.0	221.0	0.759	107	Dep
PC32	1.5	96.2	0.691	240	Dep
PC33	0.0	54.6	0.574	545	Eros/Trans
PC34	0.0	40.7	0.709	448	Eros/Trans
PC4	0.0	176.0	0.678	190	Dep
18	0.0	210.0	0.708	187	Dep
23	3.0	155.0	0.721	2244	Dep
71	0.0	10.0	0.365	402	Eros/Trans
403	8.0	175.0	0.823	358	Dep

3.2 Sediment Deposition Zones

Using bathometric maps, sites were classified as erosional, transitional or depositional based on mud DBD theory (Rowan *et al*, 1992). Lake Ontario was used as an example of how the theory worked in a large lake system and using this method it was shown that a new approach could be taken to collecting the minimum number of cores from a lake to obtain the maximum data (Rowan *et al*, 1995). Figure 3.8 shows the sediment distribution in Lake Ontario as predicted by the mud DBD theory.

Figure 3.8: Erosional, transitional and depositional areas within Lake Ontario with core locations.

3.3 Sediment Accumulation Rates

The mean SAR for the whole lake, erosional and depositional zones in $g^{\cdot}m^{-2}a^{-1}$ is shown on Table 3.2. The mean mass sediment accumulation rate as determined in this study, by Joshi *et al*, 1993 and by Thomas and Kemp (1972a) are shown on Table 3.2.

TABLE 3.2

Mass Sediment Accumulation Rates for Basins within Lake Ontario

Basin	**King**	**Joshi *et al*,1993**	**Thomas *et al*, 1972**
Niagara	287	346	114
Mississauga	358	40	139
Rochester	161	103	309
Mean Rate($g^{\cdot}m^{2\cdot}a^{-1}$)	269	84	221

The calculated value from the present study for the whole lake is a value of 269 $g^{\cdot}m^{-2\cdot}a^{-1}$. For calculations within each of the basins one data point -Stn23 in the Mississauga Basin was omitted. This value was 10 times higher than other mid-lake cores and therefore we can only assume the core had been disturbed. For sub basin calculations this core was not used. Joshi *et al* ,1994 determined mass sedimentation rates for three basins within Lake Ontario using cores taken in 1981. His value for the Rochester Basin was 103 $g^{\cdot}m^{-2\cdot}a^{-1}$ while the average in this thesis was 161 $g^{\cdot}m^{-2\cdot}a^{-1}$ for three cores. His station 403 had a rate of only 40 $g^{\cdot}m^{-2\cdot}a^{-1}$ while this thesis reports a rate of 358 $g^{\cdot}m^{-2\cdot}a^{-1}$. There is a better agreement in sedimentation rates if one compares his rate of 346

$g \cdot m^{-2} \cdot a^{-1}$ for his 9 cores within the Niagara Basin (7 are inshore -erosional) to this paper's value of 287 $g \cdot m^{-2} \cdot a^{-1}$ for 6 cores(5 are classed erosional). Thomas *et al*, (1972a) calculated sedimentation rates of 114, 139 and 309 $g \cdot m^{-2} \cdot a^{-1}$ for the Niagara, Mississauga and Rochester basins. The representative basin averages are similar for this paper and Thomas *et al*, 1972a (216 $g \cdot m^{-2} \cdot a^{-1}$ as compared to 221 $g \cdot m^{-2} \cdot a^{-1}$.)

To estimate the total fine grained sediment accumulated in one year this average was multiplied by the area of the depositional zones.

Surface Area 19,800 km^2 -whole lake
Surface Area 8,949 km^2 -depositional area
Depositional = 216,000 $kg \cdot km^{-2} a^{-1}$ x 8949 =1,932,984,000 $kg \cdot a^{-1}$
Erosional + Transitional= 10,851 x 313,000= 3,396,360,000 $kg \cdot a^{-1}$
1 ton= 907 kg
Depositional= 2,131,000 $tons \cdot a^{-1}$
Erosional and Transitional= 3,744,000 $tons \cdot a^{-1}$

The erosional and transitional zone estimate of sedimentation rate, however, has a larger uncertainty attached to it. The total lake accumulation of fine sediment is therefore estimated to be 5,800,000 tons per year. The depositional estimate of 2.1 million tons is equivalent, within an uncertainty limit, of that estimate calculated by Thomas and Kemp (1972a), of 2.28 million tons of fine-grained sediment accumulated in the main part of Lake Ontario each year. Thomas also calculated individual sedimentation, with 1.64, 0.41 and 0.22 million tons accumulating in the Rochester, Mississauga and Niagara basins respectively.

4.0 Discussion

Dating the cores gives an indication of the time and changes when anthropogenic contaminants have been deposited in the sediment. In Figures 3.3 to 3.7, the sediments have been dated and it can be seen that in Figures 3.4 (Core 403) and Figure 3.5 (PC 32) that the top 10 cm have been deposited in the last 80 years. Figure 3.5 (O 18) shows that in the last 80 years 30 cm of sediment have been deposited. Sedimentation is constant and slow and therefore we would expect porewater s to be undisturbed by sedimentation-erosional processes. The only figure (Figure 3.7) showing a spike (PC 33) occurs at 3 to 4 cm indicating the reliability of the rest of the core data. If there was a need to look for the increase in trace metals in the sediments and noting that the main depositional time for industrial contaminants was 1940 to 1970, the depth to find increased trace metals would be 5 to 20 cm in core O 18 (Figure 3.5).

From Murray-Morden , 1994 and Niagu *et al*, 1996, it is ascertained that the distribution of trace metals within a lake sediment profile and spatial distribution through the basin was not homogeneously distributed. Trace element distribution should be inversely proportional to SAR. In the shore zones the metal concentrations are much higher in the water column than the concentrations in the deeper basins (Nriagu, et al, 1996). In the sediment porewaters Murray-Morden, 1994 found that in general, concentrations of metals were higher in the deeper basins. Concentrations of isotopic lead are higher in the deep basins then the shallow shore zones. This can be seen in examining the profiles of D2 (Figure3.3) and Stn 403 (Figure 3.4). No deposition of lead isotopes is occuring near the shoreline.

The use of the mud DBD theory has been shown to be useful in predicting sediment distribution, the location of undisturbed sedimentary records, and in the extrapolation of core data to the area within the mud DBD. If researchers are looking for an area to study anthropogenic inputs of metals, the defined depositional area of the lake as indicated by the DBD theory would delineate the best area and save both time and money. In this study six cores were taken from the depositional zone. Rowan *et al*, (1995) recommended that to optimize the sampling effort 7 cores should have been taken from the depositional zone in order to estimate the mean MSAR and the total sediment accumulation.

Appleby (1993) stated that the CIC and the CRS models give the same results at sites where the unsupported ^{210}Pb profile does not deviate significantly from a simple exponential decline with depth, indicating constant sedimentation. The profiles from Lake Ontario exhibit this simple exponential decline and therefore the CIC model was determined to be appropriate.

Appleby (1993) felt that a better understanding is needed of the partitioning of radionuclides in hydrological systems between the aqueous and particulate phases. Advection and diffusion transport processes are dependent on other processes such as chemical interactions and the kinetics of sorption as well as the sedimentation rate. These processes may vary at different stages in the transport of a contaminant. Predictive models of catchment/lake systems as a whole are needed to provide a yardstick against which to assess lake sediment records. Models such as Mckay et al, 1994, used the sediment accumulation rate to calculate the water to sediment transfer of a contaminant. His constant rate model describes the chemical dynamics of a lake ecosystem as illustrated by the PCB distribution in Lake Ontario.

5.0 Conclusion

In this large lake catchment system of Lake Ontario, it appears that the sedimentation rate, although varying throughout the basin, is sufficiently low, constant and undisturbed. An assumption can be made: the diffusive transport of tritium and chloride in the porewaters is independent of the sedimentation processes.

CHAPTER 4

Tritium Diffusion in Sediment Porewaters

1. Introduction

Effective management of our aquatic resources requires a knowledge of long-term environmental data. There is a need to have a knowledge of the baseline conditions and the natural variability. In this case, the previous chapters have created the baseline of knowledge to help understand the changes that are occurring. Chapter one defines the hydrological balance of tritium in the system and chapter two defines the area of sedimentation and rates of sedimentation within the basin. Chapter two also demonstrates that the sediment cores had not been disturbed.

Over time, ionic concentrations will change as a result of chemical interactions within the sediment and solute transport across the sediment via advection and/or diffusion. The objective of this chapter is to evaluate the downward flux of contaminant movement by looking at (quantifying) the change of tritium with depth and the upward groundwater contaminant movement as described by chloride.

This chapter is divided into three sections. In the first section we look at how the solutes are moving with regards to diffusion and advection in a large lake basin by examining the distribution of chloride and tritium in the porewaters of sediment cores. The second section addresses the solute diffusion processes as quantified in laboratory experiments of bromide and tritium. Laboratory experiments were used to obtain the parameter values for the in situ cores taken throughout the lake basin.. The third section looks at the tritium porewater profiles and looks at the change in concentration gradient with depth and its relation to tritium input from anthropogenic sources (reactors). This chapter will also look at solute movement with regard to dispersion.

1.1 Background

1.1.1 Tritium

Tritium is produced naturally (Craig & Lal, 1961) and by nuclear power stations. Natural tritium and tritiated water from a nuclear power plant are continuously released to the atmosphere and then scavenged by precipitation. Tritium concentrations above the natural level are observed both in water vapor and in rainwater in the vicinity of a reactor site (Tokuyama & Oonishi,1996). This elevated tritium is observed in runoff (concentrations in rivers near a reactor site have elevated tritium-Chapter 2). Tritium from the Lake Ontario watershed outflows through the St. Lawrence River, and is evaporated, diffused and radioactive decayed.

In the saturated sediment zone, water is isolated from the atmosphere and the tritium concentration declines due to radioactive decay: the original tritium concentration of 100 TU drops to 50 TU after 12.3 years. The concentration of tritium in water is expressed by the ratio of T atoms to H atoms:

a ratio of **T/H = 10^{-18}** is defined as **1 tritium unit (TU)**

Tritium is also expressed as bequerels /liter or curies.

$0.12\ \mathrm{Bq{\cdot}L^{-1}} = 1\ \mathrm{TU}$ and $37 \times 10^{9}\ \mathrm{Bq} = 1\ \mathrm{Curie}$

Bomb testing increased tritium levels to almost 1000 TU in Canada in 1963. Levels in Lake Ontario had dropped to 120 TU at the time Pickering A nuclear powered generating station started. A time chart has been created showing the tritium emission data for Lake Ontario (Figure 2.8). The time of startup is known as well as the rate of decay of the contaminant. The baseline tritium level in the lake in 1971 when Pickering started up was 120 TU. If there were no industrial emissions from Pickering and Darlington we would expect levels closer to that of Lake Erie (56 TU). If there had been no anthropogenic sources in any of the Great Lakes, the natural production of TU in the lake would have been 5 TU (Mazor, 1991).

The hydrogeologic variables have been assessed and a tritium balance shows the reliability of that data in Chapter 2. This chapter discusses the diffusive transport of tritium.

1.1.2 Chloride

Chloride has been used as a natural tracer for decades by hydrologists due to its non-reactive nature. In this chapter the chloride in the porewaters of Lake Ontario sediments will be examined. Chloride is subject to transport across the sediment-water interface by diffusion, and mixing processes. Chloride has also been observed to be upwardly mobile by advective and/or diffusive processes from bedrock (Harvey, 1995; Drimmie in prep.). The origin of chloride in deeper lake sediments is assumed to be brackish and saline sedimentary formation waters (Frape, 1989, 1991).

Chloride is also being added to the ecosystem by the process of winter road salting. While the amount added must be large, the concentration of chloride in the lake in 1992 (average value 22.5 $mg.L^{-1}$ is equivalent to that level observed in 1970 (O'Connor and Mueller,1970).

The inclusion of chloride porewater data aids in the interpretation of the tritium data. The stability of the chloride porewater data indicates the reliability of the tritium porewater data.

1.1.3 Other Studies

The first study on the diffusion and accumulation of chloride and sodium in Lake Ontario sediments was by Lerman and Weiler, 1970. They calculated diffusion coefficients for chloride of 10^{-5} $cm^{2}\cdot sec^{-1}$. Their calculations were based on only the top 30 cm of core.

Another paper by Stiller *et al*, (1975), evaluated the transport of water through the sediments of Lake Kinneret using tritium fallout as a tracer. They used tritium to calculate the advective fluxes into the lake and found that it was negligible in the hydrologic balance. Studies concerned with the transport of major ions from deep source systems into the shallow Quaternary sediments of the area have been undertaken (Desaulnier *et al*., 1981, 1988). The land based studies have shown an upward diffusion of ions such as chloride and sodium in association with an isotopically light water (-17 to -18 delta SMOW).

Porewater chemistry, measured in a series of piston cores taken in 1990 by Drimmie and Frape (personal communication), showed an upward diffusive flux of chloride and sodium. Evidence suggests sedimentary formation brines are the source. Porewater chemistry taken from a nearshore core (W1AA -see data in appendix) found concentrations of 4,000 $mg\cdot L^{-1}$ chloride and 52 $mg\cdot L^{-1}$ bromide (Drimmie and Frape, 1995, Frape, 1991).

Siegel *et al*, (1990), have also shown that ground-water flow systems exist in the bedrock formations located along the margins of Lakes Erie, Ontario and Michigan which may be discharging saline waters, carrying heavy metals, to the lakes. Metals in groundwater input to Lake Ontario could be greater than the transport of heavy metals into the Lake from surface contaminants.

1.1.4 Diffusion

Throughout a large lake basin, it is generally assumed that diffusion is the dominant process controlling the movement of ions such as tritium and chloride into the sediments (either upwards or downwards) . This is because advection needs a hydraulic gradient as a driving force (Freeze and Cherry,1979) and it is generally assumed to be negligible or very low away from shore on the lake (especially such a large lake as Lake Ontario). Another physical process that controls movement could be the bioorganisms present in the top layers of the sediment. From ^{210}Pb analyses of the cores taken, the top mixing layer (the zone of biological/physical activity) is almost non-existent in the sediment cores (1 to 2 cm in a few cores) (Chapter 3). It can be assumed that below the zone of physical disturbance the molecular diffusion is the dominant transport process. Molecular diffusion is transport due to concentration gradients**.**

Molecular diffusion originates due to the thermal kinetic energy of the solutes. The diffusion coefficient in a porous medium is smaller than in pure liquids primarily because collision with the solids of the medium hinders diffusion. (Domenico and Schwarz, 1990). Table 4.1 shows the free solution diffusion coefficients for major ions found in groundwater (D_o values taken from Li and Gregory, 1974 and table from Harvey, 1995). Harvey adjusted the D_o coefficient to the mean annual temperature of Hamilton Harbour.

Table 4.1

Free Solution and Effective Diffusion Coefficients

Ion	$D_o[8°C]$ $(cm^{2}\cdot sec^{-1})$ x 10^{-6}
Na	8.1
K	12.0
Ca	4.8
Mg	4.6
Cl	13.0
Br	13.0

For mass transport of these ions Fick's first law that states that chemical mass flux is proportional to the gradient where:.

$$J_{di} = - D_e \frac{dc}{dx_i} \quad \frac{\text{mass of solute [M]}}{\text{unit area of porous medium x time } [M/L^2 \text{ x } T]} \qquad (4\text{-}1)$$

where D_e is the effective diffusion coefficient $[L^2/T]$ for a porous medium. The effective diffusion coefficient is defined as the product of the free-solution diffusion coefficient, D_o, and a constant which is the porosity divided by the tortuosity (τ) of the porous medium (Greenkorn and Kessler, 1972).

$$D_e = \tau D_o \text{ where } 0 < \tau < 1 \quad \text{(Bear, 1972)} \qquad (4\text{-}2)$$

Tortuosity is defined as the ratio of the length of a flow channel for a fluid particle to the length of a porous medium sample. The solute diffuses through a network of tortuous paths. For sands this number ranges from 0.56 to 0.8 (Bear, 1972). For the clayey silt sediments in Lake Ontario the number is close to 1 (Karickhoff,1985). Therefore as tortuosity decreases the diffusion coefficient should increase. Lerman,1979 states that in porous fine grained sediments (most of the Lake Ontario cores), dispersion is equal to molecular diffusion.

In the groundwater-sediment porewater system, if the solutes in the flow system are nonreactive and the rate of sediment accumulation is slow compared to rates of diffusion (Lerman,1979), the concentrations of solutes can be described by a one-dimensional, advection-diffusion equation incorporating decay for radioactive solutes. Thus dividing through by porosity:

$$\delta C/\delta t + U(\delta C/\delta t) - D(\delta^2 C/\delta z^2) + KC = 0 \qquad (4\text{-}3)$$

where C(z,t) is the concentration of solute at each depth (z) in the interstitial water, $D = \alpha V + D_e$ (effective diffusion coefficient) for a solute in porous media, U the rate of groundwater advection expressed in meters per year, and K the radioactive decay constant. A method for estimating low rates of groundwater inflow and outflow through the bottom sediments was developed and tested by Cornett et al, 1989. Figure 4.1 shows the simulated distributions of unreactive solute in waters with different advective flows. Groundwater flow upward into the lake is defined as positive. The straight line indicates steady state.

Figure 4.1 from Cornett et al, 1989 shows that steady state profiles of ^3H are significantly different in flow systems when $U>0$ (flow into lake), $U=0$ (no flow-diffusion only) and $U<0$ (flow out of the lake).

Figure 4.1: Simulated distribution of unreactive solute in waters with different advective flows (Cornett,1989).

2.0 Tritium Porewater Profiles

2.1 Results of Sampling and Analyses

Sediment and pore-water samples were obtained by the methods as outlined in Chapter 1 section 4.3. They were taken from locations as marked on Figure 4.2.

The samples that were not immediately sectioned were kept frozen until centrifugation to obtain the porewaters. The cores taken were usually in the range of 50 cm length ; there were however, 3 cores taken that were longer extending to 300 cm (PC 44, 46 and 52) .

It was expected that the tritium concentrations would resemble one of the "classic" diffusive profiles shown on Figure 4.1. However, the tritium porewater profiles in Figures 4.3, 4.4 and 4.5 show variability.

These variations need to be assessed. The first thought was there could be a problem with analytical variability. Figures 4.3, 4.4 and 4.5 show the error associated with the analyses. While some of the variations might be attributed to analytical error, the majority cannot. If one looks at the chloride changes with depth we can see that the resulting porewater profiles do not contain the tritium concentration variation. Changes in concentration are not reflected in chloride values. The two porewater profiles (chloride and tritium for the same core) behave in a separate manner. The diffusion profile cannot be smoothed out taking into account the error margins.

2.2 Data Correlations

On plotting these observed concentrations, it was noted that profiles PC 32 and 33 showed similarity (Figure 4.6).

The similarity is not random and the data must be behaving in this manner due to systematic process (more especially for the top 10 cm) and each of the longer profiles (Figure 4.5) show a spike at approximately 150 cm.

It is necessary before the discussions of results can be made, to know that this data is indeed real and that there could be no analytical-sampling problems which could have resulted in these pore-water perturbations.

2.3 Profile Variability

In the procurement of these samples three methods of sediment coring were used (previously described). Samples were collected primarily by benthos coring -gravity method. The first question addressed considered a probability that the sediment porewater could have been contaminated with lake water. Figures 4.3, 4.4 and 4.5 show both chloride and tritium in the porewaters.

First, if tritium had diffused into the core there would have been a concentration in the top few centimeters equivalent to lake water concentrations. It would not be possible to have a low tritium at 9.0 cm followed by a 2 times higher concentration at 12.0 cm (Figure 4.33-PC 32). This figure also shows that the chloride concentrations were stable with depth.

Laboratory experiments by Chant and Cornett, 1991, show experimentally in a worse case scenario of gytta (92 to 95 % water) coring, that the redistribution of a radioactive label as a result of coring, extrusion and sectioning was observed to a depth of only 5 cm in the inner core sections. Their experiments examined the possibility of smearing the radioactive label downwards into the core during coring. Smearing alters porewater and solid profiles so that the gradients calculated from the core profiles are less than those occurring in-situ in the sediments.

Another smearing experiment was conducted on Lake Erie cores (Chant, personal communication) . In this case the overlying water was spiked with ^{137}Cs and ^{22}Na and the core was sectioned to ten centimeters. Figures 4.7 a & b shows both the ^{137}Cs and ^{22}Na concentrations found with depth. In all cases the effect of smearing has disappeared by 2 cm.

The next stage after coring was the sectioning. In most cases this was completed immediately after the sample was taken. The sectioned sediment was stored in a refrigerator for the duration of the sampling cruise and upon arriving back was placed in a freezer until centrifugation. The moisture content of the core sections was first measured before the sample was processed. Each sample was centrifuged in a polyethylene tube. Tubes were not reused but thrown out. The porewaters were placed immediately into a glass scintillation vial and the sediment dried and put into a plastic cup. These porewaters were then sent to the Environmental Isotope Laboratory (Waterloo) for analysis.. Figure 4.8 shows that there is very little correlation between the moisture content of the core and the tritium porewater concentrations.

The next sections will evaluate 1)the diffusive porewater profiles of tritium and chloride as observed in laboratory experiments, 2)modelling attempts to define a diffusive parameter and 3) the question of what process could be occurring to account for these perturbations.

3.0 Laboratory Diffusion Experiments

Previous chapters have outlined the baseline knowledge of tritium in Lake Ontario. In order to understand the processes of diffusion within these lake sediments and attempt to understand the distributions observed and the processes operating, four cores were spiked with tritium and bromide to simulate the conditions in Lake Ontario. The laboratory experiments were designed according to Van Rees *et al.,* 1991. They developed a laboratory method for measuring D_S (molecular diffusion coefficient) in interstitial waters of sediments. They estimated diffusion coefficients of tritium using the reservoir method and evaluated it with other techniques for measuring diffusion coefficients. Their method showed similar results to other techniques and was more efficient and less time-consuming and therefore these experiments were conducted in the same manner.

3.1 Methods

The initial trial used a column of sediment from Lake Erie. This core was used because it was available and the sediment lithology was similar to Lake Ontario. With this column the methodology was tested, evaluating such variables as flow rates, sample collection, analysis and cutting and porewater extraction methods. No results were compiled for this trial run.

The four cores used for the diffusion experiments were taken from the locations shown on Figure 4.2. The four cores were PC 4 (75 cm), Stn 23 (55 cm), D 2 (60 cm) and O 18 (50 cm). Bromide and tritium spikes were added to the top of the cores. Bromide was added at a concentration of 1000 $mg\cdot L^{-1}$ and tritium was added at a concentration of 4000 $Bq\cdot L^{-1}$. The lake concentrations are lower (25 $mg\cdot L^{-1}$ for chloride and 10 $Bq\cdot L^{-1}$ for tritium). Bromide was used as a tracer because its free solution diffusion coefficient is similar to chloride. Chloride is present in the porewaters at varying concentrations so it could not be added as the tracer. No density affects would be present and the ionic strength increase reflects little change in the activity coefficient (Freeze and Cherry, 1979).

The flow volume was set at 3.6 $ml\cdot day^{-1}$. The diameter of the columns was 7.15 cm and the average height of solute tracer maintained over the sediment was 2.1 cm (84 mls volume over the sediment). This constant head was maintained by adding 3.6 mls/day of spiked solution by means of a variable low-speed pump. A drilled hole at 2.1 cm height maintained the outward flow into a sampling vial(concentration of spiked solution could be monitored and maintained at constant concentration with this method). Lids were placed on the top of the columns to prevent evaporative losses of the reservoir solution. The experiment was placed in a cold room maintaining a temperature of 6° C.

In this method the tritium and bromide concentrations were maintained at their original input concentration in the overlying reservoir. The tritium and bromide diffused into the four sediment columns (Figure 4.9).

At the end of the sampling period (six weeks), the reservoir solution was removed and the columns were frozen . The cores were cut up into 1 cm sections to 10 cm, 2 cm sections to 40 cm, 5 cm sections to end. Each sample was centrifuged to separate the porewater from the sediment. The porewaters were counted for tritium and measured for bromide. Moisture contents were determined for each sample.

Activities of tritium were measured on the Packard 1550 liquid scintillation counter using 1 ml of sample and 5 mls of cocktail and a count time of 3 min.. The bromide samples were measured using a double junction specific ion electrode.

3.2 Models

Estimated diffusion coefficients were calculated from the FORTRAN computer code originally created as FIN1FIT by E. Sudicky (1992) and modified by J. VanderKwaak (1993). DIFFIT is an analytical solution for a one-dimensional diffusive transport in a finite length column with first-type boundary conditions giving C=C0 at X=0 and C=CL at X=L. This solution uses non-linear least-squares fitting of concentration verses distance data. An estimated diffusion coefficient is input for preliminary iteration and the program calculates the best fit to the input observed data.

3.3 Results

Four cores which had been taken in June 1992 were used in the laboratory experiments to look at the diffusion of tritium in a controlled experiment. Each core was to be representative of a Lake Ontario core (Figure 4.2). The D-2 core was taken near Darlington and changed in lithology from sand to silt. The O 18 core was taken from the Rochester basin and was silt. The PC 4 core was chosen because it was thought to come from the Niagara River area but later data showed that it had come from the Rochester Basin. The core Stn 23 was taken from the middle of the lake and was silty.

3.3.1 Laboratory Concentration Profiles for Tritium and Bromide

Laboratory concentration profiles of bromide and tritium as they diffused through cores 0 18, and Stn 23 can be seen on Figures 4.10 a,b and 4.11 a,b and D 2 and PC 4 can be seen in the appendix. A compilation of the results can be seen on Table 4.2.

Tritium and bromide are both non reactive tracers and we would expect very little retardation. Therefore the effective diffusion coefficient as calculated would be the product of tortuosity and the free solution diffusion coefficient. The effective diffusion coefficient for the laboratory experiments are summarized on Table 4.2.

TABLE 4.2

Calculated Effective (D_e) Tritium and Bromide Diffusion Coefficients

Core	**^{3}H (cm$^{2\cdot}$sec^{-1})**	**Br (cm$^{2\cdot}$sec^{-1})**	**n**
Stn 018	1.05×10^{-5}	0.72×10^{-5}	0.7
Stn 023	0.67×10^{-5}	0.67×10^{-5}	0.62
Stn D2	0.45×10^{-5}	0.68×10^{-5}	0.35*
Stn PC4 (data not used)	9.3×10^{-5}	18.0×10^{-5}	0.68

Avg. Diffusion Coefficient (018, 023 & D2) (D_e)	**0.7 x 10^{-5}**	**0.69 x 10^{-5}**	**.58**
Free Solution (D_o)	1.4 x 10^{-5} (5 C)	1.15x 10^{-5} (4C) Chloride	

*- porosity change within core: from 0-14 cm=0.18 and from 14 to 60 = 0.46

Diffusion measurements of tritium have a complexity that was first addressed by Wang *et al*, 1952. They measured the diffusion of small amounts of deuterium hydroxide and tritium hydroxide in ordinary water and at several temperatures. They talked about structure of water, mechanisms of self diffusion, dipole orientation, viscous flow and moments of inertia. This thesis cannot address these complexities, only give the results of laboratory experiments and compare these to in-situ measured real profiles at different points in the lake.

It is known from Wang *et al*, 1952 that the free diffusion coefficient is 2.13 x 10^{-5} $cm^{2}\cdot sec^{-1}$ at 20 C and 1.39 x 10^{-5} $cm^{2}\cdot sec^{-1}$ at 5 C. The laboratory experiments were completed at about 6° C.

If we look at the coefficients for bromide we see similar results for cores 018, 023 and D2. All the coefficients are calculated to be less than the free solution coefficient for chloride.

Another laboratory investigation by Desauliers *et al*, 1988. of nonreactive solute transport in low-permeability glacial clays gave effective diffusion coefficients ranging from 6 x 10^{-6} to 13 x 10^{-6} $cm^{2}\cdot sec^{-1}$ for chloride. This range is similar to the ranges calculated for Lake Ontario sediments.

4.0 Modelling of Porewater Profiles

In an attempt to model these porewater profiles for tritium and chloride, three models were used. The program DIFFIT was used to determine effective dispersion coefficients for tritium . The profiles for tritium diffusion with time were corrected for decay to obtain the appropriate fit. To look at the profiles of chloride in the porewaters, DIFFIT was used if the profile seemed to be diffusive in nature and if it looked like there was some upward advection of chloride, the program FIN1FIT was used. FIN1FIT has a component of velocity with the dispersion coefficient. Another program SUPER1D (Sudicky,1992) was used to determine the time-variable concentration. With this program the time verses profile was obtained.

4.1 Results

4.1.1 Tritium

Figures 4.12 and 4.13 show the observed verses the calculated tritium profiles for two cores taken in Lake Ontario. Figure 4.12 (PC 31) is representative of the short cores while figure 4.13 (PC 52) represents the long cores. The term C/Co is a measure of the porewater tritium over the initial tritium concentration in the lake (76 TU). In both cases there is a downward trend and a match using a curve that follows mid line; we cannot directly match points of observed to calculated data.

An attempt was made to model all the profiles for tritium and chloride and results are shown on Table 4.3. It summarizes the range of diffusion coefficients as measured in several areas of Lake Ontario by porewater tritium and chloride profiles. These values are more like best guesses however they have been kept as an indicator of expected values and are reasonably consistent. In the following table n is porosity.

TABLE 4.3

Calculated Effective (D_e) Diffusion Coefficients for Sediment Porewaters

Core	**^{3}H (cm$^{2\cdot}$sec^{-1}) downwards**	**Cl (cm$^{2\cdot}$sec^{-1}) upwards**	**Velocity Term**	**Velocity**	**n**
PC31	1.15×10^{-5}	0.85×10^{-5}	1.0×10^{-6}	0.31 m/yr	.69
PC32	1.1×10^{-5}			no velocity	.63
PC33	0.68×10^{-5}	0.47×10^{-5}	0.83×10^{-6}	0.26 m/yr	.55
PC34	1.1×10^{-5}	0.6×10^{-5}	$.48 \times 10^{-6}$	0.15m/yr	.48
PC44	9.6×10^{-5}			sewage	
PC46	9.6×10^{-5}	0.66 x 10-5			
PC52	9.6×10^{-5}				
Stn 403	$.17 \times 10^{-5}$				.71
Stn 71	3.8×10^{-5}				.27
W1AA		1.5×10^{-5})	little data		
Free Coeff.	1.4×10^{-5} -5°C	1.15×10^{-5}			
Harvey	1.1×10^{-5}				
Avg PC31,33,34	1.0×10^{-5}	0.64×10^{-5}			
Avg (all)	2.7×10^{-5}	0.64×10^{-5}			
Avg. Lab 018,023,D2	0.70×10^{-5}	0.69×10^{-5} (Br)			

The “best fit” was used to define the effective diffusion coefficient. In three cores (PC 31, 33, and 34) the tritium is diffusing downwards at a rate very similar to the rate defined by the free water tritium coefficient (Wang *et al*, 1952). Figure 4.12 is an example of the short core. The average in-situ value of PC 31, 32 and 34 is calculated to be 1.1 x 10^{-5} $cm^{2\cdot}sec^{-1}$ as compared to 1.4 x 10^{-5} $cm^{2\cdot}sec^{-1}$. The tritium is diffusing at a rate slower than the free coefficient and the tortuosity values indicate that this is reasonable. Note also Harvey (1995) used 1.1 x 10^{-5} $cm^{2\cdot}sec^{-1}$ as his diffusion coefficient used in his Hamilton Harbor model calculations. The average coefficient for the great lake sediments can be given as 1.1 x 10^{-5} $cm^{2\cdot}sec^{-1}$ but respect must be given for the variability of this number within an individual core and throughout the lake basin.

The longer cores (PC 44, 46 and 52) as illustrated in Figure 4.13 (PC 52) have a larger diffusion coefficient (decay corrected-9.6 x 10^{-5} $cm^{2\cdot}sec^{-1}$). PC 44 is located next to a sewage outflow pipe from Hamilton and the variability in the data probably reflects a variability in the outflow concentrations(speculation). The moisture data for these long cores was lost and therefore there can be no interpretations on lithology changes throughout the core and determinations of porosity.

4.1.2 Chloride

Porewater concentrations of chloride were also measured in the sediment porewater profiles. When the only processes affecting the chloride profile are downward diffusion, then the profile becomes a straight line and concentrations at depth reflect the lakewater concentration (Figure 4.14).

Downward diffusion of chloride exists within two cores only (PC 32 and Stn 403). The free coefficient for chloride at 4 C is 1.15 x 10^{-5} $cm^{2\cdot}sec^{-1}$. If the tortuosity of the sediments is closer to one as defined by (Karickhoff, 1985) and the porosity 60% as averaged in the PC cores it would be expected that the chloride diffusion coefficient would equal 0.7 x 10^{-5} $cm^{2\cdot}sec^{-1}$. Upwards diffusion of chloride is occurring in the sediment cores PC 31, PC 33, PC 34, PC 46 and W1AA. Their calculated diffusion coefficients are shown in Table 4.3. Figure 4.15 is an example of the concentration of chloride increasing with depth, and it can be speculated that there is groundwater moving upwards through the sediments by diffusion. Figure 4.16 shows the core locations for each sediment profile having upwards diffusion of chloride.

As discussed earlier chloride is moving up from a bedrock source (a variety of Salina containing waters). The resulting calculated diffusion coefficient (0.64 x 10^{-5} $cm^{2}\cdot sec^{-1}$), that was averaged from the cores containing upwards diffusion of chloride (PC 31, PC 33, PC 34 and PC 46), is similar to that calculated for PC 32 and Stn 403(downwards diffusion of chloride-0.7 x 10^{-5} $cm^{2}\cdot sec^{-1}$ and the lab coefficient for bromide (0.67 x 10^{-5} $cm^{2}\cdot sec^{-1}$). This would indicate that advection is not a component in any of these areas. An equilibrium profile of diffusion with advection is best observed at W1AA close to shore near Niagara Falls area. There is insufficient data to calculate a velocity but the diffusion coefficient is faster than predicted. The advective flow of groundwater should not be ignored because low rates of groundwater inflow (<1m /year) could significantly alter the pore water profile and the calculation of solute fluxes into the lake.

As discussed in earlier in this section, two cored areas-the center of the lake (Stn 403) and PC 32 showed no upwards diffusion. With Stn 403 it would be expected from a hydrological viewpoint that no upwards diffusion would be found. However, PC 32 is close PC 33 and which shows upward diffusion. This suggests that upward diffusion of chloride is variable and a predication of where it is occurring would be difficult.

4.2 Discussion

The diffusion coefficients for bromide as determined in the laboratory and the in situ diffusion coefficient for chloride as determined in the lake sediments have similar values.. This indicates similar behavior. Chloride is diffusing in a “classic” manner (smooth profiles as shown in Figure 4.1).

Laboratory and in situ tritium values as determined in lake sediments are not similar. Tritium is not behaving in a “classic” manner. Lake sediments have a faster diffusion of tritium then expected from laboratory measurements. Therefore tritium in the lake moves downwards at about 15% faster diffusion than lab.

5.0 Tritium Porewater Profiles: Correlation with Emissions

5.1 Introduction

This section looks at the diffusive porewater profiles of tritium as observed through the basin and evaluates the processes that could be occurring to account for the perturbations that occur within the data set.

It was expected that the tritium concentrations would resemble a diffusive curve as shown in the laboratory results (Figures 4.10 and 4.11). It was seen in Figures 4.3, 4.4 and 4.5 that the tritium porewater concentration profiles showed variability and did not have the smoothed (dispersed) profiles. However, on plotting these observed concentrations, it was noted that profiles between PC 32 and 33 showed similarity (Figure 4.6) especially in the first 10 cm.

5.2 Short Cores

It was thought that the variations in the tritium porewater concentrations could be due to the emission inputs. Figure 4.17 shows the tritium emission data as procured from PNGS on a monthly basis. Data was obtained directly from Ontario Hydro. The tritium to water data was used directly and the tritium to air data was modified by 60%. There is an assumption from Chapter two that 60% of the tritium released to the air ends up in the lake by direct transfer, precipitation and runoff. This monthly input data base of tritium to water and tritium to air was then plotted against the tritium data.

The emission peaks follow the same pattern as the tritium profiles PC 32 and PC 33, particularly for the first 12 cm and 12 months. The data was transformed into C/Co because the model FIN1FIT required this data as the input function to obtain an effective diffusion coefficient. The lake water concentration was a constant input function. The following figure (Figure 4.18) shows the increased data correlation using this type of plotting. This figure plots the C/C_o data for each cm depth with the emission data.

Plots of PC 30 and PC 31 also show similarity. It should be remembered that these cores are located close to the Rochester Basin- therefore at an increased distance from the source. The data as a ratio of C/Co was correlated with the emission data on a monthly basis. Table 4.4 shows the data and the correlation between the cores.

TABLE 4.4

Correlation of Emissions with Porewater Tritium

	PC30	PC31	PC32	PC33	Stn 403	Stn 71
Regression	0.78	0.86	0.79	0.94	0.68	0.66

The best correlation occurs at PC 33 with a factor of 0.95 between data points, PC 31 shows a correlation of 0.86 and PC 30 and 32 show a correlation of 0.78 . Other porewater profiles such as Stn 403 and Stn 71 also show a weaker correlation of 0.68. It should be noted that PC 31 shows a high correlation with emission data from the other end of the lake. PC 31 actually monitors the ups and downs of the emissions for a longer length (ie. peaks and valleys are similar to 20 cm).

Figures 4.19 and 4.20 show a regression between data sets PC 31 and PC 33. The regression for PC 33 is 0.9 while for PC 31 its 0.86.

5.3 Long Cores

Three sediment cores were taken to a depth of 300 cm; these are PC 44, 46 and 52. Looking at these longer profiles (Figures 4.21, 4.22 and 4.23), a spike at 150 cm was prevalent in all three cores.

In the next step, the model OB51 developed by Sudicky, was used to help define the diffusion profile for PC 52. Figure 4.23 (mid Rochester basin) shows a comparable observed vs. calculated diffusion profile The decay corrected values were plotted for different times and the coefficient which best described the observed profile was 9.5 x 10^{-5} $\text{cm}^2\text{sec}^{-1}$. Looking at the time values it was apparent that 150 cm corresponded to 15 years. The emission data calculated by year from PNGS, showed a peak in 1978 -15 years from the time of coring Another "spike" occurs at 50 cm and corresponds to the peak of 1988 (approximately 4 years) in the emission records. These two pieces of evidence gave an indication that the tritium was diffusing at about a rate of 10 cm per year. Figure 4.23 shows the two peaks. The two other long cores, Figures 4.21 and 4.22 also showed a peak at about 150 cm. Their data is more variable: the variability in PC 44 can be explained by its location near Hamilton sewage outflow area.

6.0 The Dispersion of Tritium within a Large Lake

Many researchers have looked at the ability of a large body of water to disperse a contaminant below a tolerance level. The ability of a body of water like Lake Ontario to disperse a contaminant such as tritium depends on the mean flow, rate of discharge, the temperature, current speed and direction, wind velocity and direction and the irregularity of the coastal system. The resulting dispersion cannot be simply defined even by complex analytical models. The system is too diverse.

Previous measurements on Lake Ontario in two locations showed only a slight variation in tritium with depth (Figure 2.4) . The analytical error of 10% could explain the differences found. The data, could however, be addressed differently. Two peaks of higher tritium concentration occur at depths of 125 m and 215 m at Stn 08 and two peaks can be found at Stn W6 at 50 m and 125 m. Tritium may move as a discreet layer for a period of time before mixing occurs. While these cannot be described as significant they do exist. Other tritium with depth data can be seen on Figure 4.24.

Tritium concentrations with depth had been measured in June 1991 at Stn 08 as shown below and also shown on Figure 2.4 mentioned previously. Stn 08 is mid lake. In July 1992 tritium with depth measurements were taken at Stn 403 also mid lake and results shown in Figure 4.24.

On August 2 1992 a large release of 2.02 PBq was released into the waters of Lake Ontario. One month after this large release, personnel from CRL were aboard the Limnos taking water samples. They were not taking samples to look for the contamination, but lakewater samples were taken at different depths at stns 625, 465 and 466 (near Stn 403 on my map). The results can be seen on Figure 4.24.

This figure shows the increased lake water concentration only 23 days after release indicating the response of the mid lake. One data point at Stn 466 taken at 15 m (the only sample taken at that depth unfortunately) shows a very large increase in tritium.. This sample was highly scrutinized for its accuracy. This data slightly substantiates the theory that tritium may move as a discreet layer within the water profile.

This large release could now be a pulse of high tritium within the porewaters beneath the lake. A coring program to look at the location of this pulse of tritium within the porewaters at different locations within the lake, might determine the time of mixing for areas within the lake and help verify the tritium porewater profile correlation with emission data.

Another researcher has discovered that a simple diffusion model was not able to describe the chloride porewater concentrations with depth (Eggenkamp,1994). He discusses the geochemistry of chlorine isotopes, diffusion and mixing. Core samples taken north of Amsterdam showed a simple but changing chloride concentrations. He tried models of three types- 1)diffusion from a constant source, 2) diffusion with constant sedimentation rate, and 3) a model accounting for varying time periods. His conclusion was that effects such as bioturbation, currents, erosion and storm event had influenced the profile concentration and that it was not possible to use a simple analytical diffusion model.

6.1 Tritium as a Tracer of Recharge and Piston Flow:Observations

It would seem that if a correlation between tritium and emissions is real that tritium must be diffusing as a piston -plug flow. Water infiltration in a sandy soil may be described as water movement in a sponge, or homogeneous granular medium. Water descends in this setting in downward moving fronts, or in a piston-like flow. In such a model of flow a layering exists, the deeper water layers being older than the shallow ones. Measurements reveal that such piston flows proceed at velocities of a few centimeters to a few meters a year (Mazor,1991).

This movement depends on the porosity of the sediment, the degree of pore interconnections (tortuosity), and in this case of the lake sediments pressure. A case study of piston flow as reflected by tritium measurements was conducted by Winslow *et al.,* 1965 . Repeated tritium measurements were made in a well and in the adjacent Mohawk river. The variations in tritium concentrations in the well followed the variations in the river.. The data revealed piston flow of the recharge water, with little smoothening by dispersion. Piston flow could be the mechanism responsible for these tritium porewater profiles observed in these Lake Ontario sediment. Although piston flow has been documented in the past, it has not been defined at such a small scale over such a large distance.

For piston flow at such a large scale, a well mixed layer would need to move to the bottom of the west end of the lake. This layer would then diffuse into the sediments. The following theory of dispersion is presented.

At the outflow of PNGS there are four discharge bays with a combined width of 9.75 m and a discharge velocity of about 200 $cm \cdot sec^{-1}$ (Ontario Hydro , 1974). The outflow is discharged from shore at surface. (The inflow is protected by groins extending 305 m into the lake and 91.4 m apart). The average velocity of the intake is 30 $cm \cdot sec^{-1}$.

Data from J. La Marre-(Ont Hydro, personal communication) indicates that PNGS keep their effluent water at a temperature always 11° C above the ambient lake level. Stratification of this heated water occurs within 300 m of the outfall and spreads out over a layer thickness of 1 to 2 m (Ontario Hydro , 1980). Simons, 1973 says that temperature stratification is sufficient to exert a significant effect on the vertical diffusion properties of flow.

Current speeds vary from 10 to 20 $cm \cdot sec^{-1}$. This translates to 8 to 20 km per day traveling time. (Klukas and Moltyaner, 1996) In their model of aquatic dispersion modeling of the 1992 tritium plume released from Pickering they noted elevated tritium concentrations up to 20 km east and 85 km west of PNGS (wind direction reversals occurred during this two week period allowing dispersal in both directions)

The horizontal scales of motions in the lakes and oceans are much greater than the vertical scales and therefore, in many cases, their effect on mixing may be considered separately. The importance of vertical diffusion cannot be neglected even though the diffusing contaminant is, for practical purposes, confined to a very thin layer. (Murthy and Miners, 1978). Anisotopic turbulence (ie turbulent eddies which are more intense in the direction of the mean flow than across it) combined with shear diffusion due to vertical sheer in the horizontal mean current, gives rise to enhanced mixing in the longitudinal direction.

It is speculated from the above discussions that tritium released to the lake will become stratified within 300 m of shore. This tritium then moves outward along the shore in the main current direction as controlled by the wind. This layer is kept stratified due to temperature -density effects. The consequence of wind stress and horizontal shear results in the dispersion of this tritium plume from the discharge area. (Lam *et al*, 1981, found that a shear diffusion model produced the best fit for observed data on Lake Ontario) The movement of this plume depends on the above listed factors. In general the currents in the western basin of Lake Ontario flow in a counter-clockwise motion.

During this time period tritium air emissions are also being blown across the lake about 60% of the time (Chapter 2) . There is an exchange of tritium in the air with the top of the lake resulting in increased tritium concentrations in this stratified layer that are proportional to the air emissions for the time period.

There is no data substantiating a tritium “plume” that could extend the width of the lake. How big this effluent plume is and what happens to it as it moves along the lake is still left open to interpretation. It would eventually be subject to cross flow which promotes the exchange between the coastal boundary layer and midlake. Csandy, 1975 states that their is a rapid and massive exchange of water associated with current reversals that in fact abruptly remove the tracer materials from the coastal layer as if a chance event suddenly annihilated them (Figure 4.25).

This depends on the frequency of storms as well as on the probability of long waves arriving at a given location. Csandy states that we do not as yet understand these process of exchange between near-shore and midlake. There are many factors which will influence the tritium plume and theories that could be defined. This thesis leaves the data as found and hopes that eventually further studies will elucidate the answer.

7.0 Final Conclusions

It is important to understand the flux between regional groundwater systems, surface waters and sedimentation processes in order to predict the fate of contaminants entering one of the larger bodies of water in the world.- Lake Ontario. This thesis has evaluated the hydrological implications of dispersion of tritium in Lake Ontario.

Without measurements and models that can assess the transport and partitioning of radioactive substances, industry will not be able to accurately assess risks from reactor releases of radionuclides. This research improves the understanding of the movement and impacts of radioactive materials discharged from CANDU facilities by providing a mass balance model of tritium for Lake Ontario. This information could be relevant to future sites of waste disposal facilities and nuclear power plants. The information from this mass balance model can be provided to regulatory agencies such as the International Joint Commission, the Atomic Energy Control Board (AECB) and the concerned public. Ontario Hydro is now adding 48% of the annual inventory of tritium to Lake Ontario. However, the average tritium in Lake Ontario in 1992 was 9.4 Bq·L^{-1}, which is much lower than the proposed interim drinking water guideline of 7,000 Bq·L^{-1} .

Tritium readily enters the hydrologic and terrestrial systems and it has been useful as a tracer in hydrogeological investigations, atmospheric, surface water and ocean studies (Rozanski, 1991). This thesis helps establish the linkage between the loading of specific chemicals and the resulting concentrations of these chemicals in the water and sediments of the lake.

The Sediment Accumulation Rate (SAR) from the ^{210}Pb analyses can be used in conjunction with whole basin models. The average calculated for this thesis was 269 $g \cdot m^{2} \cdot a^{-1}$. This rate will address the sorption component of the advective/dispersion equation and could improve the linkage between erosion control (sedimentation) and the water quality program. In conjunction with Rowan's mud depositional boundary theory (Rowan *et al*, 1995) and data from this study, a prediction was made on the sediment distribution within Lake Ontario and the location of undisturbed sedimentary records.

Tritium diffusion through the clayey silts of lake Ontario was defined by laboratory and in-situ sediment cores. The in-situ effective diffusion coefficient was determined to be 1.0 x 10^{-5} $cm^{2} \cdot sec^{-1}$ which is slightly slower than the free water coefficient of 1.39 x 10^{-5} $cm^{2} \cdot sec^{-1}$. Tritium is moving through the system at a rate less than diffusion.
The results from the modelling of the porewater concentrations of tritium inputs into Lake Ontario shows that in the case of a large body of water overlying sediments, that it is not possible to model diffusion with a simple one dimensional analytical diffusion model. Effects such as bioturbation, erosion and sedimentation rates, currents, storm events, advection and a variable input of contaminant by anthropogenic sources could all influence the diffusion profile to some degree.

Chloride inputs into Lake Ontario sediments by upwards and downwards diffusion and this data can be modelled by a one-dimensional model. Results indicated similar values for upwards diffusion of chloride in lake sediments to the diffusion obtained by laboratory methods- 0.64 x 10^{-5} $cm^{2}\cdot sec^{-1}$.

Our resources must be used wisely and consideration should be made for the implications of increased industrialization along the shores of our lakes and rivers that empty into this large body of water. Whether or not Lake Ontario will remain a viable resource for citizens of Canada and the United States will depend on our ability to work together to protect the ecosystem and our health.

Appleby, P.G. and F. Oldfield, The calculation of Lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment, Catena, Vol. 5, 1-8**,** Braunschweig, 1978.

Appleby, P.G., Forward to the lead-210 dating anniversary series, Journal of Paleolimnology 9**;** pp. 155-160, 1993.

Anderson T.W. and C.F.M. Lewis, Postglacial water-level history of the Lake Ontario Basin, Quaternary Evolution of the Great Lakes, edited by P.F. Karrow and P.E. Calkin, GAC special paper 30, 1985.

Bear, Dynamics of fluids in porous media, New York, American Elsevier, 764 p., 1972.

Binford, M.W., J.S. Kahl, and S.A. Norton, Interpretation of ^{210}Pb profiles and verification of the CRS dating model in PIRLA project lake sediment cores, Journal of Paleolimnology 9**,** pp. 275-296, 1993.

Blais, J.M., J. Kaliff, and R.D. Evans, Evaluation of ^{210}Pb dating in lake sediments using stable Pb, Ambrosia pollen, and ^{137}Cs, McGill University Limnology Research Centre**,** Contribution # 336, 26 pp., 1994.

Broecker, W.S., Hung Peng, T., & Ostlund, G. The distribution of bomb tritium in the ocean, Journal of Geophysical Research, **91**(C12), 14, 331-14, 344, 1986.

Brown, R.M. , A review of tritium dispersal in the environment, CEC Publication, EUR 12540EN ISPP5, Brussels, Belgium, 1989.

Chant,L.A. and R.J. Cornett, Smearing of gravity core profiles in soft sediments. Limnol. Oceanogr. 36: 1492-1498 , 1991.

Chant, L.A., W.J.G. Workman, K.J. King and R.J. Cornett, Tritium concentrations in Lake Ontario, AECL Research, Chalk River, Cog-93-484, RC-1149, 1994.

Cornett,R.J., L.A. Chant, and D. Link, Sedimentation of Pb-210 in Laurentain Shield Lakes, Water Pollution Research, Vol. 19#2, 97-109, 1984.

Cornett, R.J. B.A. Risto, and D.R. Lee, Measuring groundwater transport through lake sediments by advection and diffusion, Water Resources Research, Vol. 25, No.8, pp. 1815-1823, 1989.

Cornett, R.J., L.A. Chant, and B.A. Risto, Arsenic transport between water and sediments, Hydrobiologia 235/236, pp. 533-544, 1992.

Craig,H. and Lal D., The production of natural tritium, Tellus XXIII, 85 , 1961.

Csanady,G.T., Dispersal of effluents in the great lakes, Water Research, Vol.4, pp. 79-114, 1970. .

Csanady, G.T., Circulation, diffusion and frontal dynamics in the coastal zone, J. Great Lakes Research, Vol. 1(1):18-32, 1975.

Desaulniers, D. E., J.A. Cherry and P. Fritz, Origin, age and movement of pore waters in argilaceous Quaternary deposits at four sites in southwestern Ontario, Journal of Hydrology 50, pp. 231-257, 1981.

Desaulniers, D.E., J.A. Cherry, and P. Fritz, Origin, age, and movement of pore water in clayey pleistocene deposits in South Central Canada, Isotope Studies of Hydrologic Processes, Northern Illinois univ. Press, Dekalb., Illinois, E.C. Perry and C.W. Montgomery (Ed.) pp. 45-55, 1982.

Desaulniers, D.E., R.S. Kaufmann, J.A. Cherry, and H.W. Bently, ^{37}Cl-^{35}Cl variations in a diffusion-controlled groundwater system. Geochim. Cosmochim. Acta 50, pp. 1757-1764, 1986.

Desaulniers, D.E. and J.A. Cherry, Origin and movement of groundwater and major ions via thick deposit of Champlain Sea clay near Montreal, Can. Geot. Journ., vol. 26, pp. 80-89, 1988.

Desaulniers, D.E., K. R. Bradbury, and J.A. Cherry, Groundwater origin, age, and long-term solute migration in the thick clayey tills of northwestern Wisconsin, Groundwater----, 1990.

Domenico, P.A. and F. W. Schwartz, Physical and Chemical Hydrology, John Wiley and Sons, 820 p., 1990.

Drimmie, R.J., S.K. Frape, M.J. Morden, R.L. Thomas, R.L. McNutt, and R. J. Bowins, Chemical inputs to Lake Ontario from saline formation water below the sediments , In Programs and Abstracts of the 35th Conference of the International Association of Great Lakes Research, University of Waterloo, Waterloo, Ontario, 1992.

Drimmie, R.J. and S.K. Frape, Stable chlorine isotopes in sediment pore waters of Lake Ontario and Lake Erie, IAEA-SM-366/17, Isotopes in Water Resources Management, 1995.

Drimmie, R. J., Geochemical and isotopic indicators of formation water brine movement into Lake Ontario and Lake Erie sediments, in prep, PhD thesis, University of Waterloo.

Eakins, J.D. and R.T. Morrison, A new procedure for the determination of Lead-210 in lake and marine sediments, International J. of Applied Radiation and Isotopes, Vol. 29, 531-536, 1978.

Eggenkamp, H.G.M., The Geochemistry of Chlorine Isotopes, Chapter 4, Theoretical fractionation of chlorine isotopes during molecular diffusion, 1994.

El-Daoushy, F. The ^{210}*Pb* global cycle: Dating and tracing applications in Low Level Measurements and their Application to Environmental Radioactivity, eds. M. Leon-Garcia and G. Madurga World Scientific Publ. Co., Singapore, pp. 224-273, 1988.

Flegal, A.R.; J.O. Nriagu, S. Niemmeyer, and K. Coale, Nature, pp. 455-458, 1989.

Frape, S.K. Interstitial waters and bottom sediment geochemistry as indicators of groundwater seepage, PhD Thesis, Queen's University, 1979.

Frape, S.K. and R.J. Patterson, Chemistry of interstitial water and bottom sediments as indicators of seepage patterns in Perch Lake, Chalk River, Ontario, Limnology Oceanography, 26(3), pp. 500-517, 1981.

Frape, S.K., Mixing of saline basinal fluids in Southern Ontario: Implications of rock-water interaction, hydrocarbon emplacement and Canadian shield brines, Water-Rock Interaction, Miles(ed.), Balkema, Rotterdam, 1989.

Frape S.K., Regional saline groundwater inputs into the shallow groundwater environment: Implications for trace metal and organic contamination, International Symposium on Groundwater issues of the Lower Great Lakes, Buffalo Association of Professional Engineers, Niagara Falls, N.Y., 1991.

Freeze, R.A. and Cherry, J.A., Groundwater, Prentice-Hall Inc., 1979.

Gadd, N.R., Pleistocene geology of the central St. Lawrence lowland: Geological Survey of Canada Memoir 359, 153p., 1971.

Goldberg, E.D., Geochronology with ^{210}Pb, symposium on radioactive dating (IAEA, Vienna) pp.121-131, 1969.

Gorman, D.J. & Wong, K.Y. , Environmental aspects of tritium from CANDU Station releases, Int. Symposium on the behaviour of tritium in the environment, California, IAEA-SM-232/49, 1978.

Greekorn, R.A. and D.P. Kessler, Transfer operations: New York, McGraw-Hill, 548p. (1972).

Gustafson, P.F., Future levels of tritium in the Great Lakes from nuclear power production, In Proceedings of the 13th Conference Great Lakes Research, pp. 839-843, 1970.

Haefeli,C.J., Groundwater inflow into Lke Ontario from the Canadian side, Scientific Series No. 9, Inland Waters Branch, Dept. of the Environment, 1972.

Haras W.S. and K.K. Tsui (Ed.), Canada/Ontario Great Lakes shore damage survey, Coastal Zone Atlas, Canadian Department of the Environment, Ottawa, Ontario, 1976.

Harvey, E., Evaluation and development of methods for hydrogeologic studies in deep lakes; Applications in the Hamilton Harbour, Western Lake Ontario, PhD Thesis, University of Waterloo, 1995.

Health and Welfare Canada, Guidelines for Canadian Drinking Wataer Quality, 4th ed., prepared by the Federal-Provincial Advisory Committee on Environmental and Occupational Health, Canadian Government Publishing Centre, Ottawa, 1989.

Hough, J.L., Geology of the Great Lakes, Univ. Illonois Press, Urbana, IL., 313 p., 1958.

Joshi, S.R., B.S. Shukla and A.G. Bobba, Lead-210 sedimentation in Lake Ontario, Environ. Geol. Water Sci., 1994.

Karickhoff, S.W.,and K.R. Morris, Environmental Sci. and Technology, 19, 51, 1985.

Kemp, A.L.W., Organic Matter in the sediments of Lakes Ontario and Erie, Proc. 12th Conf. Great lakes Res., pp. 237-24, 1969.

Klukas, M.H. and G.L. Moltyaner, Aquatic dispersion modeling of a tritium plume in Lake Ontario, AECL-11526, 1996.

Kramer, J.R., Chemistry of Western Lake Ontario, Great Lakes Research, Pub. No. 9, pp21-29, 1962.

Krishnaswami,S., D. Lal, J.M. Martin and M. Meybeck, Geochronology of lake sediments, Earth Planet Sci. Letter 11, pp 407-411,1971.

Lam,D.C.L. , C.R. Murthy and K.C. Miners, An inverse problem approach to modeling coastal effluent plumes, Adv. Water Resources, Vol.4, pp. 185-188, 1981.

Lee, D.R., A device for measuring seepage flux in lakes and estuaries, Limnol. Oceanogr., 22, pp.140-147, 1977.

Lee, D.R., J.A. Cherry, and J.F. Pickens, Groundwater transport of a salt tracer through a sandy lakebed, Limnol. Oceanogr.,25, pp.45-61, 1980.

Lerman,A., and R.R. Weiler, Diffusion and accumulation of chloride and sodium in Lake Ontario sediment, Earth and Planetary Science Letters, Vol. 10, pp.150-156, 1970.

Lerman, A., Geochemical Processes: Water and Sediment Environments-Wiley, New York, 481 pp., 1979.

Li, Y. and S.Gregory, Diffusion of ions in sea water and in deep-sea sediments, Geochimica et Cosmochimica Acta, 38, p. 703-714, 1974.

Lickly, T.D., Blanchard, F.A., & Takahashi, I.T., Survey of tritium radioactivity in Lake Huron surface water, Environmental International, 9, 221-224, 1983.

Mackay, D., Sang,S., Vishos, P., Diamond, M., Gobas, F., and D. Dolan, A rate constant model of chemical dynamics in a lake ecosystem: PCBs in Lake Ontario, J. Great Lakes Res., 20(4), pp. 625-642, 1994.

Martini, I.P. and J.R. Bowbly, Geology of the Lake Ontario Basin: A review and outlook, Canadian Journal of Fisheries and Aquatic Science, Vol.48, pp. 1503-1516, 1991.

Martini I.P. and J.K.P. Kwong, Nearshore sediments of Lake Ontario with special reference to the Presqui'ile-Wellengton Bay area, Ontario Geologic Survey, open file Rep. No. 5557, 99 pp, 1985.

Mazor, E., Applied chemical and isotopic groundwater hydrology, Open University Press, Great Britain,1991.

McBride, M.S. and H.O. Pfannkuch, The distribution of seepage within lakebeds, Journal Research U.S. Geol. Surv., 3, pp. 505-512, 1975.

McNutt, R.H., S.K. Frape, and P. Dollar, A strontium, oxygen, and hydrogen isotopic composition of brines, Michigan and Appalachian Basins, Ontario and Michigan, Applied Geochemistry 2, pp. 495-505, 1987.

Michel, R.L., Tritium inventories of the world oceans and their implications, Nature 263, 103-106, 1976.

Mudroch, A, Distribution of major elements and metals in sediment cores from the Western Basin of Lake Ontario, J. Great Lakes Research, 9 (2), pp 125-133, 1983.

Muller,E,H. and V.K. Prest, Glacial lakes in the Ontario Basin: in Karrow, P.F., and Calkin, P.E. eds., Quaternary Evolution of the Great Lakes; Geological Association of Canada Special Publication 30, 1985.

Murray Morden, M.J., Trace element geochemistry of Lake Ontario sediments and porewaters, M.Sc. Thesis, University of Waterloo, 1994.

Murthy,C.R. and K.C. Miners, Turbulent diffusion processes in the Great Lakes, Environment Canada, Scientific Series no. 83, 1978

Nriagu,J.O., H.K.T. Wong, and R.D. Coker, Particulate and dissolved trace metals in Lake Ontario, Water Research, Vol. 15, pp 91-96, 1981.

Nriagu, J.O., G. Lawson, H.K.T. Wong and V. Cheam, Dissolved trace metals in Lakes Superior, Erie, and Ontario, Environ. Sci. Technol. 30**,** pp. 178-187, 1996.

O'Connor, D.J. and J.A. Mueller, A Water quality model of chlorides in Great Lakes, Journal of the Sanitary Engineering Division, Proceedings of the American Society of Civil Engineers, pp. 955-975, August 1970.

Oldfield, F. and P.G. Appleby, Empirical testing of ^{210}Pb-dating models for lake sediments, in Lake Sediments and Environmental History, University of Minnesota Press, edited by E.Y. Haworth and J.W.G. Lund, pp.405, 1984.

Ontario Hydro, Hydrologic investigations Lake Ontario. Report on nearshore currents at Pickering generating Station, 1973. Hydraulics Studies Dept. Publication, Ontario Hydro, Toronto, Ontario, 1974.

Ontario Hydro, Lake Ontario Pickering Generating Station analysis of thermal plume surveys conducted 1971 to 1979, Rep. No. 80072, Hydraulics Studies and Development Dept. (prepared by A.A. Arajs, Toronto, Ont.), 1980.

Ontario Hydro. Annual summary and assessment of environmental radiological data for 1991, HSD-HP-92-9, Health and Safety Division, Toronto, Ontario, 1992.

Ostlund, H.G., North Atlantic gyre studies and associated projects, Tritium Laboratory Data Report 13, University of Miami, Rosentiel School of Mar. and Atmos. Sci., Florida, 1984.

Prest, V.K., Quaternary geology of Canada, In R.J. W. Douglas (Ed.), Geology and economic minerals of Canada, Geol. Surv. Can. Econ. Geol. Rep. No. 1, pp. 676-764, 1970.

Robbins, J.A., J.R. Krezoski and S.C. Mozley, Radioactivity in sediments of the Great Lakes: postdepositional redistribution by deposit-feeding organisms, Earth Planet Sci. Letter 36, pp 325-333, 1977.

Robbins, J.A., Geochemical and geophysical applications of radioactive lead, in Biogeochemistry of Lead in the Environment, Part A, Vol. 1A, Elsevier Scientific Publishers, edited by J.O. Nriagu, pp. 285-303, 1978.

Robbins, J.A. and L.R. Herche, Thirty years of ^{210}Pb dating: successes and problems, Abstract in Heavy Metals in the Environment-International Conference, Toronto, 1993.

Rowan, D.J., J. Kalff and J.B. Rasmussen, Estimating the mud deposition boundary depth in lakes from wave theory, Canadian Journal of Fish Aquatic Science 49, pp. 2490-2497, 1992.

Rowan, D.J., J. Cornett, K. King and B. Risto, Sediment focussing and ^{210}Pb dating, Journal of Paleolimnology, 13, pp. 107-118, 1995.

Rozanski, K., Gonfiantini, R., & Araguas-Araguas, L., Tritium in the global atmosphere; distribution patterns and recent trends, IAEA, Vienna, Journal of Physics, Nuclear and Particle Physics, 17(suppl), S523-S536, 1991.

Rukavina, N.A., Nearshore sediments of Lakes Ontario and Erie, Geoscience Can. 3; pp.185-190, 1976.

Schell, W.R. and M.J. Tobin, ^{210}Pb dating using the CRS-MV model with historical data to test and evaluate accuracy, Proc. 3rd Intl. Summer School, Huelva, Spain**,** pp 14, 1993.

Seigel,D.I., S.K. Frape, A. Martini, R.J. Drimmie, and R. L. Thomas, Heavy metal transport to the Great Lakes by natural ground-water discharge: An initial evaluation, Proceedings Can-Am Water Resources Assoc. Conference on Great Lakes Issues, Toronto, 1990.

Sellinger,C.E., Groundwater flux into a portion of eastern Lake Michigan, J. Great Lakes Res., 21 (1), pp. 53-63, 1995.

Sly, P.G., Sedimentology and geochemistry of modern sediments in the Kingston Basin of Lake Ontario, J. Great Lakes Research, 10(4), pp. 358-374, 1984.

Stiller, M. I.Carmi, and K.O. Munnich, Water transport through Lake Kinneret sediments traced by tritium, Earth and Planetary SCience Letters, 25, pp.297-304, 1975.

Thomas, R. L., A.L.W. Kemp, and C.F.M. Lewis, Report on the surficial sediment distribution of the Great Lakes, Part I-Lake Ontario, Geol. Surv. Can. Paper 72-17, 52 pp., 1972a.

Thomas, R. L., A.L.W. Kemp, and C.F.M. Lewis, Distribution, composition, and characteristics of the surficial sediments of Lake Ontario, J. Sediment Petrol., 42, pp. 66-84, 1972b.

Thomas,R.L., R.K. McMillan, D. Keyes, J. R. Bowlby, C.F.M. Lewis, and A.A. Mohajer, Recent faulting along the postulated extension of the St. Lawrence Rift System in Lake Ontario, unpublished,1994.

Torgersen,T. Z. Top, W.B. Clarke, W.J. Jenkins, and W.S. Broecker, A new method for physical limnology-tritium-helium 3 ages - results for Lake Erie, Huron, and Ontario, Limnol. Oceanogr. 22, pp.181-193, 1977.

Van Rees, K.C.J., E.A. Sudicky, P.S.C. Rao and K.R. Reddy, Evaluation of laboratory techniques for measuring diffusion coefficients in sediments, Environmental Science and Technology, 25, pp. 1605-1611, 1991.

Wang, J.H., and C.V. Robinson, I.S. Edelman,
Seif-diffusion and structure of liquid water. III Measurement of the self-diffusion of liquid water with ^{2}H, ^{3}H and ^{18}O as tracers, Vol. 75 466-470, 1952.

Weiler, R.R., The interstitial water composition in the sediments of the Great Lakes:1) Western Lake Ontario, Limnol. Oceanogr., 18, pp.918-931, 1973.

Winslow, J.D., H.G. Stewart Jr., R.H. Johnston and L.J. Crain, Groundwater resources of eastern Schenectudy County, New York, with emphasis on infiltration from the Mohawk river, State of New York Conservation Department Water Resources Commission Bull., 57, 148, 1965.

Winter, R.C. Numerical simulation of steady state three-dimensional ground water flow near lakes. Water Resources Res. 14, pp. 245-254, 1978.

Wood, M.J. & Workman, W.J.G., Environmental Monitoring of tritium in air with passive diffusion samplers, Fusion Technology, 21(2), Part 2, 529-535, 1992.

APPENDIX

```
*****************************************************************
*                                    *
*          1-D DIFFUSION TEST                  *
*          NONLINEAR LEAST SQUARES ANALYSIS              *
*                                    *
*          TEST OF LEAST-SQUARES ALGORITHM:              *
*          MArch 1 1996: tritium-Stn 403 14cm           *
*                                    *
*****************************************************************


PHYSICAL PARAMETERS
===================
CONCENTRATION AT X=0:                 1.00
CONCENTRATION AT X=XL:                 0.760
MODEL EVALUATED AT TIME:               0.526E+06
ESTIMATED DIFFUSION COEFFICIENT:        0.230E-02
NUMBER OF TERMS IN SERIES:                 8


NOTATION
========
SSQ:        RESIDUAL SUM OF SQUARES
S.E.COEFF.:  STANDARD ERROR OF ESTIMATED PARAMETER
T-VALUE:     COMPUTED T-STATISTIC FOR ESTIMATED PARAMETER
ITER:        ITERATION NUMBER IN LEAST-SQUARES ANALYSIS


INPUT DATA
==========
 I      DIST     CONCENTRATION

 1      0.0000      1.0000
 2      2.0000      0.9500
 3      4.0000      0.8200
 4      6.0000      0.8100
 5      8.0000      0.8000
 6     10.0000      0.8200
 7     12.0000      0.7600
 8     14.0000      0.7600
```

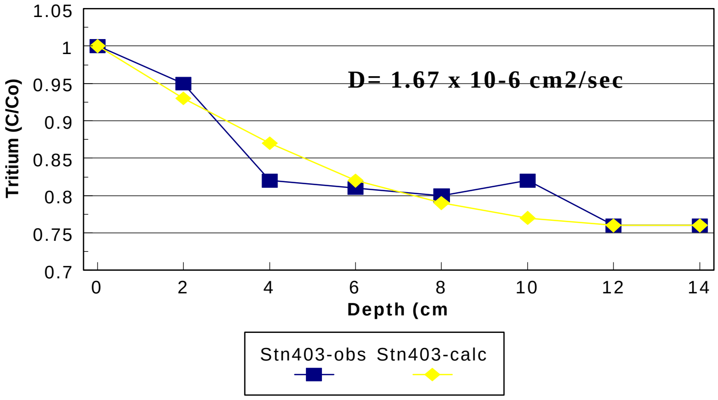
```
ITER     SSQ          D
 0    0.25513E-01  0.230E-02
 1    0.25509E-01  0.446E-03
 2    0.25509E-01  0.450E-03
 3    0.15115E-01  0.146E-03
 4    0.59217E-02  0.104E-03
 5    0.58808E-02  0.102E-03
 6    0.58800E-02  0.102E-03
 7    0.58799E-02  0.102E-03
 8    0.58799E-02  0.102E-03



NONLINEAR LEAST-SQUARES ANALYSIS, FINAL RESULTS
==============================================
                                      95% CONFIDENCE LIMITS
NAME        VALUE      S.E.COEFF.  T-VALUE       LOWER        UPPER
   D      0.10E-03      0.79E-05    13.       0.835E-04     0.121E-03

 DIST       CONC-OBS    CONC-FIT    RESIDUAL
 0.0000      1.0000      1.0001     -0.0001
 2.0000      0.9500      0.9333      0.0167
 4.0000      0.8200      0.8730     -0.0530
 6.0000      0.8100      0.8242     -0.0142
 8.0000      0.8000      0.7899      0.0101
10.0000      0.8200      0.7701      0.0499
12.0000      0.7600      0.7619     -0.0019
14.0000      0.7600      0.7601     -0.0001

 END OF PROBLEM
==============
```



Porewater profile for Stn 403-Tritium