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Probabilistic Spill Occurrence Simulations and Quantitative Water Quality Risk Analysis for Chemical Spill Management

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PROBABILISTIC SPILL OCCURRENCE SIMULATIONS AND
QUANTITATIVE WATER QUALITY RISK ANALYSIS FOR
CHEMICAL SPILL MANAGEMENT

by

WEIHUA CAO

M.A.Sc. in Environmental Applied Science and Management

Ryerson University, Canada, 2009

A dissertation

presented to Ryerson University

in partial fulfillment of the
requirement for the degree of

Doctor of Philosophy

in the program of

Civil Engineering

Toronto, Ontario, Canada, 2013

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AUTHOR'S DECLARATION

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ABSTRACT

WEIHUA CAO, Ph.D, Civil Engineering, Ryerson University, Toronto, 2013

Thousands of inland chemical spills occur as a result of accidents or natural disasters each year in the world and threaten human health and the environment. More than 700 recorded inland chemical spills involving more than 1,000 types of chemical occur every year in Southern Ontario, resulting in multiple environmental impacts. Eleven regional municipalities involving 77 municipalities had experienced chemical spills in the period of 1988-2007. The majority of these chemical spills occurred at industrial plants, while pipe/hose leaks accounted for the highest proportion of total chemical spills, resulting in the largest portion of chemical spills causing surface water impacts.

A comprehensive spill management planning framework is proposed to facilitate the development of municipal spill prevention, control, and emergency response plans. In order to develop a spill management framework, simulation models termed MMCS (MATLAB-based Monto Carlo Simulation) and EMMCS (Extended MMCS) that characterizes temporal and spatial randomness and quantifies statistical uncertainty have also been developed. The MMCS model simulates the probabilistic quantifiable occurrences of inland chemical spills by time, magnitude, and location based on North America Industry Classification System (NAICS) codes, while the EMMCS model quantifies the risk of drinking water quality violation due to inland chemical spills. The models can also quantify aleatory and epistemic uncertainties through integrated bootstrap resampling technique.

Benzene spills into the St. Clair River Areas of Concern are used as a case study to demonstrate the models. The probabilistic occurrences of various NAICS codes are found to be 1.2 to 5.1 over a 10-year period. The violation-causing NAICS-based spill occurrences and the associated risks of drinking water quality impairments at the Ontario's intakes are found to be less than 1.4 and 37%, respectively. No drinking water quality is found to be impaired at the Michigan intakes. Uncertainty analysis indicates that simulated spill characteristics can be described by lognormal distributions and the NAICS-based risks of violation at the Ontario's intakes are Weibull distributed. A hypothetical case, benzene spills in the Mimico Creek watershed is used to investigate the possibility of spill characteristic transfer from one area to another area.

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DEDICATION

This paper is dedicated to my parents. I would give my especially appreciations to my father who gave me his ultimate spirit supports for the successful completion of this research before his passing away.

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CHAPTER 1 INTRODUCTION

1.1 Background

Thousands of oil and chemical spills occur each year worldwide through accidents or natural disasters and bring a great potential to harm human health and impact water, air and land and their associated terrestrial and aquatic species, which has been well documented by Tagatz (1961), Hutchinson *et al.* (1974), McKinley *et al.* (1982) and Shales *et al.* (1989). As defined by several environmental legislation, a spill is a form of ‘discharge’ (Ontario Water Resources Act s. 1(1) & s. 1(3)(b) 1990; Ontario Environmental Protection Act s. 91(1) 1990; Environmental Protection Act, Ontario Regulation 675/98 Part I), ‘deposit’ (Canadian Fisheries Act s. 34 1985), ‘release’ (Canadian Environmental Protection Act s. 3(1) 1999), or ‘an uncontrolled, unplanned or accidental release’ (Canadian Environmental Protection Act s. 193 1999). It enters the environment ‘from or out of a structure, vehicle or other container’ (Ontario Environmental Protection Act s. 91(1)(b) 1990). Spills are characterized as harmful in terms of their ‘deleterious’ effects (Canadian Fisheries Act s. 34 1985), ‘impairment’ to water quality (Ontario Water Resources Act s. 1(3) 1990), and ‘adverse effects’ (Ontario Environmental Protection Act s. 1(1) 1990; Environmental Protection Act, Ontario Regulation 675/98 Part I). A spill occurrence is ‘abnormal in quality or quantity in light of all the circumstances’ (Ontario Environmental Protection Act s. 91(1)(c) 1990) and represents a failure in system, education, engineering, regulation, enforcement or packaging (Castle 1999).

Inland spills have been identified as one of the major sources of pollution of the Great Lakes

(Cheng 2010) and pose great threats to water quality there. Unlike tanker spills in oceans, inland spills originate from industrial and municipal lands (Li 2005), including production sites, local product stores and transportation corridors and can be transported by groundwater and surface water, and air to another location. They can occur for a number of reasons and situations, such as equipment failure or human error, and may cause impairment of drinking water quality, contamination of surface water and groundwater, destruction of freshwater invertebrates and vertebrates, and disturbance of fish habitats and wildlife populations, especially in spawning areas (Li & McAteer 2000). The types of spill that are of most concern are those of toxic substances which can directly or indirectly be deposited into watercourses through several different routes, such as airborne dispersal, leaking (e.g. ground/underground tank and landfills), discharge, overflow, and so on (Environment Canada 1997). Spills in large quantity could acutely elevate certain toxic chemicals at water intakes (Cheng 2010). Even in small quantities spills could affect the long-term toxicity levels in ambient waters.

Federal facilities, agencies, boards and crown corporations are involved in a wide variety of activities that may result in the use or production of any of the following materials containing potentially deleterious substances: biomedical and other hazardous wastes, food and food processing wastes, sewage and water treatment facility effluent, laboratory chemicals, garage and machine shop fuels, oils and lubricants, paint and printing shop solvents, paints, dyes, and deicing chemicals for aircraft and airport grounds, and hydrocarbons from aircraft fueling operations (Environment Canada, 1997). All activities using or producing these materials anywhere may cause inland spills and discharges into the environment. Therefore, multi-jurisdictional responsibilities for inland spill management are shared by all levels of government

(federal, provincial, and municipal), industries, and individual Canadians (Environment Canada, 1998).

1.2 Relevant Legislation

Federal, provincial, and municipal governments have enacted relevant legislation for water resource protection. The regulations prescribed by these acts mainly focus on maintaining the integrity of the natural environment and preventing any adverse effects to the natural environment by spills (Li, 2002d). The Canadian Environmental Protection Act (1999) is the principal federal legislation which aims at prevention of toxic substance release (s. 64) and require pollution prevention (s.57 and s.291) and environmental emergency plans. The Emergency Management and Civil Protection Act (1990) requires every municipality to prepare an emergency plan which includes a procedure to deal with emergency situations such as hazardous spills. The Canada Fisheries Act (1985 c F-14) addresses spills by prohibiting the depositing of all deleterious substances in any type of waters frequented by fish or in any other place under circumstances where the substances could enter the water (s.36(1) and (3)).

The Ontario Clean Water Act (2006) was enacted to ensure water sources are protected from non-point sources of pollution, such as spills. Municipal drinking water quality standards are set out in the Ontario Drinking Water Quality Standards (Ontario MOE 2002) under the Ontario Safe Drinking Water Act (2002). The enactment of this act also forces industries to be more attentive to spill management resulting in a decreasing trend of spill frequency over the last 20 years. Chemical concentrations under the maximum acceptable concentration (MAC) are deemed safe for lifelong human consumption of drinking water (Health Canada 1996). The

Ontario Spills Bill Part X, under the Ontario Environmental Protection Act (1990), requires that spills or discharges that may have an impact on the environment or may generate waste requiring special disposal must be reported (s. 92(1)). The Ontario Municipal-Industrial Strategy of Abatement (Ontario MOE, 2007c) regulations require industries that are prone to toxic releases to report spills, and implement spills prevention and contingency plans as well. Municipal sewer by-laws restrict the quantity and quality of the disposal of hazardous spills into the sewer system, which travel through the infrastructure as runoff into the catch basins and sewers.

There have been some initiatives targeting spill prevention, preparedness, and management in Canada. For instance, the Environmental Emergencies Branch of Environment Canada has developed the Priority List for chemical spills to focus on research and development efforts for the most frequently spilled and harmful chemicals (Fingas *et al.*, 2000). The top priority chemicals have been focused on through the development of analytical techniques and the preparation of chemical-specific response manuals. It has been suggested that ten years is an appropriate time period to re-evaluate the Priority List because spill statistics may change with time due to the changes of chemical use and transportation patterns. In Ontario, the Ontario Spill Action Centre (SAC) was established to record spill events and other urgent environmental events on a daily basis, initiate or coordinate a response as required, and provide support to municipalities. The City of Toronto has been obliged to mitigate water contaminants from spills in order to preserve the water quality of Lake Ontario under the Great Lakes Water Quality Agreement between the Canadian and American governments.

Most large municipalities across Canada, such as the cities of Toronto, Ottawa, and Hamilton,

and the regional municipalities of York, Peel, and Durham, regulate spill reporting systems in their Sewer Use Bylaw. For instance, the Sewer Use Bylaw No. 2011-56 of The Regional Municipality of York (2011) requires,

In the event of a spill to a sewage works, the person with charge, management or control of the substance spilled or the person who caused or permitted the spill shall immediately notify the Region, provide any information with respect to the spill which the Region advises it requires and complete any work the Region may require to mitigate the spill.

The person who gave notice shall do everything possible to stop and contain the spill, protect the health and safety of the public and adjacent occupants, minimize damage to property, protect the natural environment, mitigate actual and potential impacts, clean-up the spill and remediate and restore the affected area to its condition prior to the spill event.

Within 5 calendar days after the first occurrence of the spill, the person who gave notice shall provide a written report on the spill to the Region containing information to the best of the person's knowledge including:

- *location where the spill occurred;*
- *name and phone number of the person who reported the spill and location where such person can be contacted;*
- *date and time of spill;*
- *substance that was spilled;*
- *physical and chemical characteristics of the spilled substance;*
- *volume of the substance spilled;*

- *duration of spill event;*
- *any relevant information regarding the cause of the spill or the circumstances surrounding the spill event;*
- *work completed, in progress and/or to be undertaken to mitigate the spill;*
- *preventative actions being taken to ensure the situation does not occur again; and*
- *any other information the Region may indicate it requires in relation to the spill.*

1.3 Research Needs

As discussed in Section 1.2, the federal, provincial and municipal acts, regulations and initiatives have targeted industrial spill prevention and management. Therefore, it is hypothesized that spill events will be decreased with time. However, hundreds of chemical spills still occur every year in Southern Ontario and present an increasing tendency for the period of 2003-2007, resulting in surface water pollution and other negative environmental impacts (Cao *et al.*, 2012), implying that industries may not well prevent, control, and management spill occurrences. For instance, benzene spills generated by various facilities in the St. Clair River Area of Concern (AOC, a site where environmental quality is significantly degraded and beneficial uses are impaired) have been reported to enter directly or indirectly into the river leading to violations of water quality at water treatment plant (WTP) intakes and justifying plant shutdowns (Cheng, 2010). Therefore, a new research is acutely needed to address the issue of effective measures on spill occurrence prevention and management in order to protect source waters and human health.

Additionally, most current spill-related research is focused on oil spills. A Tactical Decision Problem (TDP) associated with oil spill cleanup operations was formulated as a general integer

program to optimize total response time to the spill over a planning horizon with an assumption of known oil type, quantity and occurrence location (Wilhelm and Srinivasa, 1997). An optimization procedure for this TDP model was developed based on an aggregation scheme and strong cutting plane methods (Srinivasa and Wilhelm, 1997). A multiperiod mixed-integer linear programming model was developed under economic and responsive criteria and coupled with oil transport and weathering model to simultaneously predict the optimal time trajectories of oil slick's volume and area, transportation profile, response resource utilization levels, cleanup schedule, and coastal protection plan with various specifications of the response time span (Zhong and You, 2011; You and Leyffer, 2011). However, although many researchers engage in developing water quality models for the investigation of the fate and transport of contaminants in source water, not enough studies on the effect of inland chemical spills on fresh water has been justified and there is a lack of models for forecasting the probabilistic quantifiable occurrences of inland spills and analyzing their risks of water quality impairments at downstream locations along receiving waters that can be used to aid decision making. Without spill occurrence prediction and risk analysis models, all decisions on spill management are lack of technical support and will lead to high costs on spill prevention and control. For instance, the lack of information of potential spill occurrence time, magnitude and location would mislead to spill management resources allocation (e.g. finance and human resources) which may cause a long response time for an emergent spill event and impairments of the environment and/or human health if the spill could not be controlled and cleaned up promptly. Therefore, it is indicated again that a new research is needed to address the origins and management of inland spills in order to protect source waters.

1.4 Research Scope and Objectives

Since the SAC spill database records the spills that occur in Southern Ontario, the research scope focuses on this area. The main objective is to develop a framework for a comprehensive inland chemical spill management strategy, which can be used to assist a municipality or a conservation authority for preventing, controlling and responding to an inland spill and protecting water resources. In order to achieve this objective, a planning tool was to be considered which includes the following components: (1) a probabilistic mathematical model for predicting inland chemical spills' occurrences by time, magnitude and location, (2) a selected water quality model for predicting the downstream concentrations of the spills along receiving waters, and (3) a quantitative risk analysis model for water quality impairment due to the spills at downstream locations along the receiving waters. This research mainly focused on the development of the planning tool, which corresponded to the research needs discussed in the previous section.

1.5 Expected Outcome

The outcome of the research is expected to be as follows:

- (1) A framework for a comprehensive inland chemical spill management plan for source water quality protection and management, which will require the models as outlined in (2) and (3); These models are not only the main components but also the technical support of the spill management plan and associated risk-informed decision making.
- (2) a quantifiable probabilistic model for simulating inland chemical spill occurrences by time, magnitude and location, and quantifying expected spill occurrence time and mass for a location, based on categories of business establishments according to type of economic

activity (process of production) defined by North America Industry Classification System codes; and

- (3) a quantitative risk analysis model for downstream water quality impairment due to inland chemical spills along a receiving water, which involves water quality modelling.

These outcomes can fill in the current research gaps mentioned in the Section 1.3. The approach of this research not only can be used by water quality practitioners to develop spill occurrence prediction models and estimate the associated risks of water quality violations along waterways, but also can be used by regulatory agencies and municipalities to make decisions on spill management in order to minimize the spills' potential that threatens source water quality and/or human health. The approach is also appropriate to assist an industry to develop spill prevention, control and management plan according to its own historical spill characteristics and regulatory requirements.

1.6 Organization

This dissertation comprises seven chapters. Chapter 1 is the introduction and overview of the dissertation. Chapter 2 reviews relevant literature, including previous works, water quality modelling concepts, probability distributions, and risk analyses. Chapter 3 describes the statistical and spatial analysis of inland chemical spills in Southern Ontario based on the Ontario SAC (Spill Action Center) and the SLEA (Sarnia-Lambton Environmental Association) databases, and mainly focuses on inland chemical spills that impact surface water quality. Chapter 4 presents the development of a quantifiable probabilistic model for simulating inland chemical spill occurrences by time, magnitude, and location, and a case study of benzene spills

in the St. Clair River AOC for model demonstration. Chapter 5 describes the development of a quantitative risk analysis model for water quality impairment at downstream locations along the receiving water, and case studies of benzene spills along the St. Clair River and Mimico Creek (hypothetical case) for model demonstration. It is clearer to state that inland chemical spills have a direct relationship upon receiving water quality. Therefore, the research was expected a unique comprehensive framework for inland chemical spill management, which not only could be used by water quality practitioners to predict the occurrence of inland spills and perform the risk analysis on source water quality impairment at downstream locations along receiving waters, but can also be used by regulatory agencies and municipalities to evaluate the effectiveness of remedial actions against inland spills and develop a comprehensive inland spill management strategy that minimizes the potential threats to human health and/or the environment (see Chapter 6). Chapter 7 concludes the study, by recommending directions for future related research, and identifying the model's limitations.

CHAPTER 2 LITERATURE REVIEW

This chapter reviews literature related to the fate and transport of contaminants in receiving waters (especially in river systems), water quality models, risk analysis, common probability distributions (PD), and some applications.

2.1 Previous Work

Inland chemical spills are considered emergent non-point water pollution sources generally not related to storm events (Li and McAteer, 2000) and pose threats to the Great Lakes basin and everywhere. Unfortunately, most spill research activities concentrate on marine spills rather than the more frequent inland spills. Recognizing the importance of inland spills in the Great Lakes, Li *et al.* (2002a, 2002b, 2002c, 2002d, 2002e, 2003) were commissioned by multi-level governments to conduct research on inland spills in the Great Lakes areas. A geocoded spill database of more than 50,000 records in Southern Ontario was developed in 2003 and subsequently used by graduate students in a number of research studies at Ryerson University. For instance, Tang (2005) developed a methodology to estimate the expected economic damage of oil spills for a large petroleum industry using an analysis approach for flood frequency.

The advantages of establishing a web-based GIS for inland spill management were identified and a basic web-based GIS framework was developed by Han (2007) to map spill locations. She studied inland oil spills in the Etobicoke District of the City of Toronto between 1988 and 2002. It was concluded that there were 1225 oil spills occurring in this district during this time. The

year of 1992 and the month of June had the highest total spills (111 and 122 spills respectively) reached the highest. Despite the unknown type of spills, gasoline is the most spilled substance followed by diesel fuel. Parking lots are the most frequent locations where spills occur followed by local roads. Han (2007) provided a planning framework for municipal oil spill management, which consisted of four major steps: (1) oil spill inventory analysis, (2) oil spill pollution prevention, (3) oil spill control measures, and (4) oil spill response and cleanup. Unfortunately, this framework lacked planning tools for achieving inland oil spill management.

Cheng (2010) studied inland chemical spills in the St. Clair River AOC and investigated the risk of a water treatment plant shutdown due to spills through the joint probability of flow and spilled mass that cause water treatment plant shutdowns. It was concluded that 891 chemical spill events happened in the St. Clair River AOC between 1988 and 2007 that spilled a total 4,661,605 kg of chemicals into this channel with the event mass ranging from 0.01kg to 2,286,000 kg. The most frequent causes were valve/fitting leak/failure, pipe line leak, and discharge/bypass to watercourse between 1988 and 2007, which account for 25, 15, and 11% of the total spill mass, respectively. The media that received spills from highest to lowest number was air, water courses and surface water, soil and vegetation, multiple media and human health and safety, while the chemical sector (47%) was responsible for most chemical spills followed by the petroleum (20%) and general manufacturing (19%) sectors. Cheng's results also showed that discharge/bypass to water courses accounts for 97% of benzene mass spilled to air, water, and soil. The log-normal probability distribution was used to describe the spill events' mass. The risk of water treatment plant shutdowns due to benzene spills over a two-year period was found to be 41% and 19% for 1988-1997 and 1998-2007 respectively. Finally, Cheng (2010) suggested risk-based spill

management criteria to evaluate the effectiveness of spill prevention and control programs.

2.2 Transport and Fate of Contaminants in Receiving Waters

Contaminants travel down slopes over land, and most often end up in surface water bodies such as a stream, river, lake, or sea. During their travel, a part of the total amount might be depleted due to evaporation or loss by adhering to surface vegetation, rocks, and soils, and deposition in surface puddles and pools (Farrar, *et al.*, 2005). The overland flow of spilled contaminants is governed by the properties of the contaminant, physical nature of the land surface and the degree of slope. Once they reach and enter surface water, such as a river or a lake, their transport and fate are affected by physical, chemical, and biological processes (Al-Rabeh *et al.*, 1989), and a number of environmental conditions (e.g. winds, waves, current, water depths, temperatures, salinities, organisms, nutrients, and chemical type). Therefore, it is very important to account for the characteristics of receiving waters. This research mainly focuses on river systems.

The most distinct characteristic of a river is its natural downstream flow. The health of a river is directly linked to the health of its surrounding watershed. The water quality in a river will deteriorate if the watershed condition deteriorates. River characteristics can change significantly over time in response to human activities and changing climate and hydrologic conditions. Rivers vary widely by morphological, hydraulic, and ecological characteristics, including slope, width, depth, flow rate, flow velocity, water temperature, sediment transport, contaminants deposition, nutrient inflows and eutrophication processes (Ji, 2008). Point and nonpoint pollution sources have caused a wide range of water quality problems and the deterioration of the ecological state in rivers. According to the U.S. EPA (2000), the key pollutants and stressors in

rivers are pathogens/bacteria, siltation, habitat alterations, oxygen-depleting substances, nutrients, thermal modifications, toxic metals, and flow alterations.

When a pollutant is discharged into a waterbody, it is subject to fate and transport processes that modify the concentration of the pollutant downstream (Ji, 2008). Advection, dispersion, and convection are three hydrodynamic transport processes. Substances in water systems can be transported by one or all of these processes. Advection refers to horizontal transport by flows, resulting in the movement of a substance downstream; dispersion is the horizontal spreading and mixing of water caused by turbulent mixing and molecular diffusion, resulting in the reduction of the substance concentration and the net transportation of the dissolved substance from the areas of high concentration to those of low concentration; and convection refers to vertical transport of water and very small pollutants in rivers and lakes. In addition, turbulent mixing that combines advection and convection mechanisms is the dominant component of dispersion in a river; longitudinal mixing leads to the substance spreading in the same dimension; and lateral and vertical mixing determines the complete mixing time of the substance across the river (Ji, 2008).

Transport currents and horizontal shears in the currents contribute to dispersion of contaminants in water column (Reed *et al.*, 1995). The advective velocity is a significant factor in the transport of the pollutant, while the flow velocity controls the travel time of the contaminant in the river. Rapid transport of the pollutant by high flow results in a short residence time and has minimal water quality problems. Conversely, slow transport of pollutants by low flow results in a long residence time and can lead to water quality problems such as oxygen depletion and drinking water impairments.

Over the past decades, mathematical models to describe the fate of contaminants have been investigated by many researchers. Al-Rabeh *et al.* (1989) discussed the transport and fate of spilled oil in surface water, which is being affected by physical, chemical, and biological processes including advection, turbulent diffusion, surface spreading, evaporation, dissolution, emulsification, vertical mechanical dispersion, photo-oxidation, biodegradation, and sinking and sedimentation, and proposed a comprehensive stochastic model, which consisted of a set of algorithms to describe these processes, to simulate the fate and transport of oil spills in surface water. Al-Rabeh *et al.* (1989) concluded that dissolution was the most active process shortly after a spill entering into a river, while photo-oxidation and biodegradation were both unimportant over the first few days. These processes also apply to the transport and fate of chemical spills in rivers.

In rivers, mass balance is a fundamental to describe the changes of a conservative substance with time, as given by Eq. (2.1). Based on this equation, Chapra (2008) proposed a water quality model to estimate the concentration of a conservative substance at various times, as shown in Eq. (2.2), whose numerator represents an Euler-method prediction of the mass in segment i of the river at a time step and whose denominator is an Euler prediction of its volume.

$$\frac{\partial(AC)}{\partial t} = -\frac{\partial(QC)}{\partial x} \quad (2.1)$$

$$C_i^{l+1} = \frac{V_i^l C_i^l + (Q_{i-1}^l C_{i-1}^l - Q_i^l C_i^l) \Delta t}{V_i^l + (Q_{i-1}^l - Q_i^l) \Delta t} \quad (2.2)$$

Where:

- A is the cross-sectional area of river, m^2 ;
- C is the concentration of a substance, kg/m^3 ;

- Q is the flow rate of river, m^3/s ;
- t is time and Δt represents a time interval, per second;
- x is a location in river or stream, m ;
- V is the volume of water, m^3 ;
- l represents a time point.

Contaminants in a water column are carried to the water floor primarily by adsorption to suspended particulates and subsequent settling. Reed *et al.* (1995) introduced a standard equilibrium partitioning theory to compute the ratio of adsorbed to dissolved concentrations, as shown in Eq. (2.3).

$$\frac{C_a}{C_{dis}} = K_{oc} C_{ss} \quad (2.3)$$

Where:

- C_a is the adsorbed concentration, kg/m^3 ;
- C_{dis} is dissolved concentration, kg/m^3 ;
- C_{ss} is the concentration of suspended particulate matter in water column, kg -particulate/ kg - water;
- K_{oc} is partition coefficient, dimensionless.

The Eq. (2.3) assumes that the duration of the release of contaminants will be short (e.g. days to months) compared to sediment diffusion times (e.g. years). Then, Reed *et al.* (1995) also suggested a one-dimensional diffusion equation for a single loading of pollutant to sediment, as given by Eq. (2.4).

$$C = M \left(\pi D_{bio} t \exp \left[-kt - \frac{z^2}{D_{bio} t} \right] \right)^{-\frac{1}{2}} \quad (2.4)$$

where:

- C is pollutant concentration to the sediment, kg/m^3 ;
- M is total pollutant mass per unit area, kg/m^2 ;
- D_{bio} is sediment bioturbation rate, m^2/day ;
- t is time, day ;
- z is depth (positive down) into the sediments, m ; and
- k is decay rate, per day.

Contaminants which sank directly to the sediments might be returned to the water column by the process of dissolution (Reed, *et al.*, 1995). The contaminants concentrations in sediment were suggested to be distributed between adsorbed and dissolved states by linear partitioning, as in the water column. The ratio of adsorbed to dissolved contaminant was also determined by Eq. (2.3).

Thibodeaux (1977) suggested a dissolution mass transfer rate model, as shown in Eq. (2.5).

$$\frac{dm}{dt} = kA_c (C_s - C_w) \quad (2.5)$$

where

- k is water phase mass transfer coefficient, $m \, day^{-1}$, which is determined by Eqs. (2.6) and (2.7)

$$\text{Laminar flow:} \quad k = 0.664 Re^{-1/2} Sc^{-2/3} CV_{\infty} \quad (2.6)$$

$$\text{Turbulent flow:} \quad k = 0.036 Re^{1/2} Sc^{1/3} C \frac{D_{AB}}{L} \quad (2.7)$$

where Re is Reynolds number; Sc is Schmidt number; C is bulk concentration, kg/m^3 ; V_{∞}

is the velocity far removed from interface, D_{AB} is molecular diffusivity of A in B, m^2/s ; and L is length of pool, m .

- A_c is the interfacial area for mass transfer at concentration C_s , m^2 ;
- C_s is the minimum contaminant concentration at the sediment/water interface and the saturation concentration; and
- C_w is ambient concentration of the contaminant in water.

The transport of contaminants from injection at a riverbank to a point downstream in the river is estimated using the distribution of the chemicals in the flow direction of the river and the distribution of the flow rate of the river. After an instantaneous contaminant enters a river, its concentration at any time and any distance downstream could be estimated by a one-dimensional equation (Hemond and Fechner-Levy, 2000), as shown in Eq. (2.8).

$$C(x,t) = \frac{M}{\sqrt{4\pi D_L t}} \exp \left(-\frac{(x - Vt)^2}{4D_L t} \right) \quad (2.8)$$

where:

- C is the concentration of conservative chemical, kg/m^3 ;
- M is the mass of chemical entered per cross-sectional area of river, kg/m^2 ;
- x is the distance downstream of entrance, m ;
- V is the average river velocity, m/s ;
- t is the time elapsed since entrance, s ; and
- D_L is the longitudinal dispersion coefficient, m^2/s , which can be estimated by Eqs. (2.9) and (2.10) (Fischer *et al.*, 1979).

$$D_L = \frac{0.011V^2 w^2}{du^*} \quad (2.9)$$

$$u^* = \sqrt{gdS} \quad (2.10)$$

Where:

- w is the width of the river, m ;
- d is the depth of the river, m ;
- u^* is the shear velocity, m/s
- g is the acceleration of gravity, m/s^2 ; and
- S is the slope of the river (dimensionless).

Typical values of D_L range from 0.05 to 0.3 m^2/s for small streams (Genereux, 1991) to greater than 1000 m^2/s for large rivers (Wanner *et al.*, 1989). Rutherford (1994) reported some D_L coefficients at particular locations and times for several rivers, such as 4.7, 111, 92.9, 316 and 1500 m^2/s in Monocacy, Yadkin, Susquehanna, Sabine, and Missouri with the velocity of 0.21, 0.43, 0.39, 0.58, and 1.55 m/s , respectively.

If chemical concentration follows first-order decay during transport downstream, Eq. (2.8) becomes Eq. (2.11) (Hemond and Fechner-Levy, 2000). At any given time t , the maximum concentration of the chemical (C_{max}) is found at a distance downstream of the entrance point (x) equal to the product of the time elapsed (t) since entrance and the average river velocity (V). At this location, the C_{max} can be determined by Eq. (2.12).

$$C(x, t) = \frac{M}{\sqrt{4\pi D_L}} \exp \left(-\frac{(x - Vt)^2}{4D_L t} \right) \exp(-kt) \quad (2.11)$$

$$C_{max} = \frac{M}{\sqrt{4\pi D_L}} \exp(-kt) \quad (2.12)$$

where k is a first-order rate constant (in per second) for chemical transformation and removal processes.

Eqs. (2.8), (2.11) and (2.12) are used under the assumption that a chemical enters a river uniformly across a river cross section. In fact, after entering a river, the chemical must travel a certain distance before its concentration becomes uniform. For a chemical released at a river bank, the length of the transverse mixing zone can be roughly estimated by Eq. (2.13) (Hemond and Fechner-Levy, 2000).

$$L \approx \frac{w^2 V}{2D_t} \quad (2.13)$$

where L is the length of transverse mixing zone (m), D_t is the transverse Fickian mixing coefficient (m^2/s), and others are the same as discussed above. For typical natural channels, the coefficient D_t can be roughly estimated by $D_t \approx \frac{w^2}{2t}$, where t is the time since the chemical was released (s). Rutherford (1994) reported some D_t coefficients in several rivers, such as 0.12, 0.038, and $3.1 m^2/s$ in Missouri, Danube, and Orinoco, respectively.

Chan (1980) examined a simple transient model for an instantaneous release of a finite amount of material recommended by the US Nuclear Regulatory Commission Guide 1.113 (USNRC, 1977) and derived various expressions for shoreline instantaneous point source discharges. The expressions for peak concentration, arrival time, departure time, and duration of passage of instantaneous point source and non-instantaneous extended-source shoreline releases are shown in Table 2.1 through Eqs. (2.14) to (2.19). Nettleton and Hamdy (1988) applied these equations to develop a water quality model - SpillMan - specifically for the St Clair River. The details of

the SpillMan model are discussed in Chapter 5.

Table 2.1: Expressions for peak concentration, arrival time, departure time, and duration of passage for instantaneous point source and non-instantaneous extended-source shoreline releases (Chan, 1980).

Instantaneous Point Source Release (IPS model)	
Spill Arrival Time	$t_a = \frac{x}{u} + \frac{4K_x}{u^2} - \frac{2}{u^2} \sqrt{4K_x^2 + 2uxK_x} \quad (2.14)$
Spill Departure Time	$t_d = \frac{x}{u} + \frac{4K_x}{u^2} + \frac{2}{u^2} \sqrt{4K_x^2 + 2uxK_x} \quad (2.15)$
Non-Instantaneous Extended-Source Shoreline (VS model)	
Spill Arrival Time	$t_a = \frac{x}{u} - \frac{2}{u^2} \left(\sqrt{4K_x^2 + 2u\bar{x}K_x} - \sqrt{4K_x^2 + 2ux^*K_x} \right) \quad (2.16)$
Spill Departure Time	$t_d = \frac{x}{u} + \frac{2}{u^2} \left(\sqrt{4K_x^2 + 2u\bar{x}K_x} + \sqrt{4K_x^2 + 2ux^*K_x} \right) \quad (2.17)$
Duration of Spill Passage	$t = t_d - t_a = \frac{4}{u^2} \sqrt{4K_x^2 + 2uxK_x} \quad (2.18)$ (replaces x by \bar{x} in VS model)
Spill Peak Concentration	$C(x = ut, y = 0, t) = \frac{M}{2\pi dt \sqrt{K_x K_y}} = \frac{Mu}{2\pi dx \sqrt{K_x K_y}} \quad (2.19)$ (replaces x by \bar{x} in VS model)

Where:

- C is the peak concentration of a spill, kg/m^3 ;
- x and y are alongshore and cross-stream coordinates, m ;

- x^* is a distance upstream and used to determine the position of the virtual source used for the prediction for extended sources, where Q is the spill discharge and T is spill release duration;
- $\bar{x} = x^* + x$, is observer distance, m ;
- M is the amount of spilled mass, kg ;
- d is the mean depth of River, m ;
- t is the time after the spill release, s ;
- u is the longshore current, m/s ;
- K_x and K_y are the dispersion coefficients, m^2/s .

Neely *et al.* (1976) developed a water quality model to predict concentration-time profiles resulting from chemical spills at any downstream locations along a small river. The model divided the river into a series of n continuous stirred flow compartments. The output from each compartment is fed into the next compartment where the concentration of the output is the same as that in the compartment. The concentration in the n th compartment at time t is expressed by Eq. (2.20). The time for the maximum concentration to reach any point downstream and the corresponding maximum concentrations for the n th compartment can be determined by Eqs. (2.21) and (2.22). This model can be used for both completely water soluble chemicals and partially soluble materials.

$$C_n(t) = \frac{M \left(\frac{Q}{V} t \right)^{n-1}}{V(n-1)!} \exp \left(- \left(\frac{k_e}{h} + \frac{Q}{V} \right) t \right) \quad (2.20)$$

$$t_{n, \max} = \frac{n-1}{\frac{k_e}{h} + \frac{Q}{V}} \quad (2.21)$$

$$C_{n, \max} = \frac{M}{V} \left(\frac{\frac{Q}{V}}{\frac{k_e}{h} + \frac{Q}{V}} \right)^{n-1} \frac{1}{\sqrt{2\pi(n-1)}} \quad (2.22)$$

where:

- C_n is uniform contaminant concentration in the n th compartment at time t (in s), kg/m^3 ;
- M is mass of contaminant released into river instantaneously, kg ;
- V is volume of the n th compartment, m^3 ;
- Q is volumetric flow rate of the river assumed to be constant through each compartment, m^3/s ;
- k_e is rate constant for the evaporation of the contaminant, m/s ; and
- h is depth of the compartment, m .

2.3 Probabilistic Distributions and Occurrences

To investigate probabilistic events of a stochastic process (e.g. spill occurrences), it is important to analyze available historical data and determine the probability distribution (PD) of observations. Many researchers have discussed the applications of linear least square, maximum likelihood, moments, and order statistics for estimating the PD parameters of a stochastic process (see e.g., Bhattacharya and Bhattacharjee, 2010; Mijić et al., 2009; Izsák, 2008; Wu, 2002; Holland and Fitz-Simons, 1982). The most common applied probability distributions in general

are listed below.

1. Normal

Normal distributions are extremely important in statistics and have been often used in the natural and social sciences for real-valued random variables whose distributions are unknown (Casella and Berger, 2001). Its probability distribution function (PDF) and cumulative distribution function (CDF) are given by Eqs. (2.23) and (2.24).

$$\text{PDF: } f_x(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right) \quad -\infty \leq x \leq \infty, \quad -\infty < \mu < \infty, \quad \sigma > 0 \quad (2.23)$$

$$\text{CDF: } F_x(x) = \frac{1}{2} + \frac{1}{2} \operatorname{erf}\left(\frac{x-\mu}{\sqrt{2\sigma^2}}\right) \quad (2.24)$$

where

- μ and σ are two parameters of the distribution, which are the mean and standard deviation of random variable, respectively. Johnson and Kotz (1970) discussed the methods of linear least square, maximum likelihood, moments, and order statistics for estimating the parameters μ and σ . Mage and Ott (1984) evaluated the methods of fractiles, moments and maximum likelihood for estimating parameters μ and σ when sampling air quality data and demonstrated that the maximum likelihood was preferred.
- $\operatorname{erf}(x)$ is an error function, where $\operatorname{erf}(x) = \frac{1}{\pi} \int_{-x}^x e^{-t^2} dt$

2. Lognormal

The lognormal distribution has been used by researchers for decades to model many kinds of environmental contaminant data. For instances, the concentrations of pH, alkalinity, chlorides,

ammonia, iron, and aluminum in river water (Dolgonosov and Korchagin, 2011), the concentrations of PM10 - particulate matter with an aerodynamic diameter lower than 10 μm - in the City of Volos, Greece (Papanastasiou and Melas, 2010), benzene and vinyl chloride spill mass in the St. Clair River AOC (Cheng, 2010), the concentrations of volatile organic compounds (Jia *et al.*, 2008), and total petroleum-hydrocarbon concentrations in soil (Salmeen *et al.*, 1995), air quality data (Mage, 1981; Georgopoulos and Seinfeld, 1982), trace metals in fish (Giesy and Weiner, 1997), radionuclide data sets (Pinder and Smith, 1975; McLendon, 1975; and Horton *et al.*, 1980), strontium-90 and other fission-product concentrations in human tissues (Schubert *et al.*, 1967). Air pollution data are more often lognormal due to atmospheric dynamics and concentration levels that are never less than zero (Goldman *et al.*, 2011). The PDF and CDF of two-parameter lognormal distribution are expressed by Eqs. (2.25) and (2.26).

$$\text{PDF: } f(x) = \frac{1}{x\sigma_y\sqrt{2\pi}} \exp\left(-\frac{1}{2\sigma_y^2}(\ln x - \mu_y)^2\right) \quad x > 0, \quad -\infty < \mu_y < \infty, \quad \sigma_y > 0 \quad (2.25)$$

$$\text{CDF: } F(X < x) = \frac{1}{2} + \frac{1}{2} \operatorname{erf}\left(\frac{\ln x - \mu_y}{\sqrt{2\sigma_y^2}}\right) \quad (2.26)$$

where

- x represents one datum of the data set (X) of the benzene spilled mass.
- $\mu_y (= \mu_{\ln(x)})$ and $\sigma_y (= \sigma_{\ln(x)})$ are the two parameters of the lognormal distribution, which are true mean and variance of transformed random variable $Y = \ln X$, respectively.

Through some software such as MATLAB built-in function, the mean and variance of a two-parameter normal or lognormal distribution can be estimated easily, but the user is required to purchase a software license.

3. Weibull Distribution

A Weibull distribution has been widely used to describe environmental contaminant data, such as the waiting time of metal cutting acoustic emissions (Polito *et al.*, 2010), air pollution concentration (Georgopoulos and Seinfeld, 1982), radionuclides (Pinder and Smith, 1975), spatial and temporal distribution of atmospheric radioactivity (Apt, 1976), and ambient ozone data (Johnson, 1979). Its PDF and CDF are expressed by Eqs. (2.27) and (2.28).

$$\text{PDF: } f_T(t) = \frac{\beta}{\lambda} \left(\frac{t}{\lambda} \right)^{\beta-1} \exp \left(- \left(\frac{t}{\lambda} \right)^\beta \right) \quad t \geq 0 \quad (2.27)$$

$$\text{CDF: } F(T < t) = 1 - \exp \left(- \left(\frac{t}{\lambda} \right)^\beta \right) \quad (2.28)$$

Where

- t represents one datum of the data set (T) of the benzene spill inter-event time.
- λ and β represent scale and shape parameters of the Weibull distribution, respectively.

The scale parameter determines the range of the distribution, while the shape parameter gives the distribution its flexibility. If $\beta = 1$, the Weibull distribution is identical to the exponential distribution.

4. Exponential Distribution

As a special case of the Weibull distribution, an exponential distribution has been widely used to describe inter-event time in engineering evaluation, such as rainfall events, floods, droughts, time to failure for certain engineering systems, and so on (Singh *et al.*, 2007). Its PDF and CDF are expressed by Eqs. (2.29) and (2.30).

$$\text{PDF: } f(x) = \lambda e^{-\lambda x} \quad x \geq 0, \lambda > 0 \quad (2.29)$$

$$\text{CDF: } F(x) = 1 - e^{-\lambda x} \quad x \geq 0, \lambda > 0 \quad (2.30)$$

where: λ is a parameter of the distribution, often called the rate parameter.

5. Gamma Distribution

The PDF and CDF of a Gamma distribution are expressed by Eqs. (2.31) to (2.34). They have been used to describe many stochastic processes, such as rainfall (Aksoy, 2000).

$$\text{PDF: } f(x) = \frac{k^\alpha}{\Gamma(\alpha)} x^{\alpha-1} e^{-kx} \quad x \geq 0, k > 0, \alpha > 0 \quad (2.31)$$

$$\text{where } \Gamma(\alpha) = \int_0^\infty x^{\alpha-1} e^{-x} dx \quad (2.32)$$

$$\text{CDF: } F(x) = \frac{1}{\Gamma(\alpha)} \gamma(\alpha, kx) \quad (2.33)$$

$$\text{where } \gamma(\alpha, kx) = \int_0^{kx} t^{\alpha-1} e^{-t} dt \quad (2.34)$$

where: k and α are scale and shape parameters of the distribution, respectively.

2.4 Risk and Risk Analysis

Risk is calculated as the joint probabilities of an occurrence of an event and its consequences and risk analysis refers to a process of the estimation of the frequency and physical consequences of undesirable events (Ricci *et al.*, 1981). It is characterized by two quantities: the magnitude of possible adverse consequence(s) and the probability of the occurrence of each consequence (Stamatelatos, 2000). Usually, risk is taken as the mean or expected value of consequences or damages expressed by the product of probability and its consequences (Ganoulis, 2009), as shown in Eq. (2.35). The risk associated with a number of events is expressed by Eq. (2.36).

$$Risk = P_i \times D_i \quad (2.35)$$

$$Risk = \sum_i P_i \times D_i \quad (2.36)$$

where P_i is probability of event i , and D_i is the consequence of event i , such as a damage.

According to Ganoulis (2009), mathematical estimations for the risks to surface water quality are intended to estimate the expected deviation from defined quality standards and possible consequences. In terms of source water quality, the magnitude of adverse consequence is treated as 1 because of the violation of water quality caused by a pollutant and therefore its risk becomes the probability of exceeding the acceptable concentration set by regulation or environmental quality standards, which is given by Eq. (2.37). Considering the concept of risk, p_F is the asymptotic limit of the ratio of number of times system fails and total number, as shown in Eq. (2.38).

$$p_F = P(C \geq C_s) \quad (2.37)$$

$$p_F = \lim_{N \rightarrow \infty} \left(\frac{N_F}{N_F + N_S} \right) = \lim_{N \rightarrow \infty} \left(\frac{N_F}{N} \right) \quad (2.38)$$

where p_F is the probability of failure of the pollutant in a steady-state system, C is the concentration of the pollutant in surface water, C_s is the standard concentration for the pollutant in surface water, N_F is number of times the system fails where $C > C_s$, N_S is number of times the system succeeds, and N is total number which is $N_F + N_S$.

It is necessary to analyze the risk of chemical spills for water quality due to their toxicity. To estimate the risk of the contamination of a river, variabilities in time and space of water quality

characteristics should be taken into consideration (Ganoulis, 2009). The following steps can be applied for analyzing the risk of source water pollution: 1) identifying risk, 2) identifying the conditions involving incidents or failures, 3) estimating risk under water quality standards. The mass balance equation for the contaminant are proposed to be used together with Monte-Carlo simulation to generate outputs in the form of frequency distributions of contaminant concentrations expected at given locations as shown in Fig. 2.1. The following statistical variations could be included: (1) probability distribution of river flow rate, (2) frequency distribution or time series of contaminant loadings (location 1 in Fig. 2.1), (3) concentration after initial dilution, and (4) frequency distribution or time series downstream using modelling (location 2 in Fig. 2.1). Statistical independence is always assumed between random variables, such as flows and contaminant loadings, although some correlation frequently occurs.

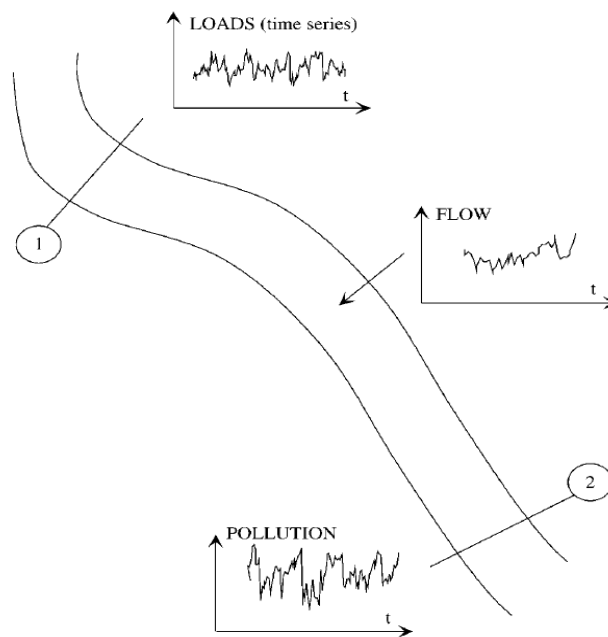


Fig. 2.1: Risk estimation of river pollution (source: Ganoulis, 2009). The concentrations of the pollutant are expressed in the form of frequency distributions at sampling location.

2.5 Model Uncertainty, Sensitivity, Calibration, and Verification

Both mechanistic models and empirical models involve physical or empirical parameters that cannot be quantified accurately and have predictive uncertainty (Tung and Yen, 2005). When a model involves parameters whose values cannot be certain, the traditional approach is to conduct sensitivity analysis by changing a parameter's value, such as ± 10 or $\pm 20\%$, from each input; this helps with an understanding of the model and avoids a mistaken impression. However, it is fundamentally meaningless to run this analysis to determine the uncertainties in the final point estimates (Thompson *et al.*, 1992). Sensitivity analysis only provides partial information needed for conducting an uncertainty analysis (Tung and Yen, 2005). Therefore, performing an uncertainty analysis could encompass sensitivity analysis. Uncertainty is a situation where an observed or calculated value may differ from the true value due to the lack of perfect information on processes, which results in risks for decision making. Mays and Tung (1992) simply defined uncertainty as the occurrence of events that are beyond control. Although uncertainty is undesirable and unavoidable, manageable uncertainty provides the freedom to make creative decisions.

Generally, the sources of uncertainty in evaluating the reliability of environmental and water resources systems or in designing the systems based on reliability include the uncertainties of nature, model structure, model parameter, data, computation, and operation (Singh *et al.*, 2007; Tung and Yen, 2005). Natural uncertainties are associated with the inherent randomness of natural geophysical processes (Tung and Yen, 2005). Since model formulation varies over a wide spectrum, ranging from simple empirical equations to sophisticated partial differential equations with computer simulations, their uncertainties reflect the inability of model or design

procedures to represent precisely a system's true physical behaviour. Parameter uncertainties could be caused by the inherent variability of inputs and parameters in time and space and the lack of sufficient data. For instance, the parameters of a PD model cannot be estimated accurately due to limited numbers of observations; an empirical equation's coefficients are developed through calibrating or fitting a model to a limited amount of sample data. Data uncertainties arise from measurement errors, inconsistency and non-homogeneity of data, data handling and transcription errors, and inadequate representation of data samples due to time and space limitations (Singh *et al.*, 2007; Tung and Yen, 2005). Operational uncertainties are associated with construction, manufacture, deterioration, maintenance, and other human factors that are not accounted for in the modeling or design procedure (Singh *et al.*, 2007). Model prediction errors can be classified into systematic and random errors (Ang and Tang, 1984). Measurement errors can also be categorized into systematic and random errors (British Standard Institution, 1998; Rabinovich 2000). Systematic errors may arise from factors that are not accounted for in the model, while random errors may be associated with the range of possible errors primarily due to sampling errors. In general, systematic errors associated with model prediction could be removed by multiplying a several bias-correction factors to or by subtracting the bias from the model output.

In order to improve the accuracy and usefulness of models, the following four problem areas that are affected by uncertainties must be addressed (Beck, 1987): (1) uncertainty about model structure or formulation, i.e., what are the basic processes involved, how are their interactions be mathematically characterized in an efficient and parsimonious manner; (2) uncertainty in the model parameters, i.e., parameter identification and calibration problems; (3) uncertainty

associated with estimates of the future behaviour of the system, i.e., aggregation of uncertainties in model structure or formulation, model parameters, and in the definition of design or decision scenario into overall estimation uncertainty; and (4) reduction of critical modelling uncertainties through carefully designed experiments and monitoring programs. Uncertainties can be categorized as either aleatory or epistemic. If the uncertainties are caused by randomness in nature, it is characterized as aleatory, while those characterized as epistemic arise from the lack of the knowledge of systems or paucity of data. It is impossible to reduce aleatory uncertainties but epistemic uncertainties could be reduced through increasing the knowledge and a longer history of quality data (Singh *et al.*, 2007; Kiureghian and Ditlevsen, 2009).

Uncertainties can be measured in terms of the probability density function (PDF), confidence interval, or statistical moments of random variables (e.g., standard deviation or coefficient of variation) of stochastic parameters (Tung and Yen, 1993). The PDF can provide the most complete and ideal description of the uncertainty features of a quantity (Tung and Yen, 2005). Confidence interval is a measure of the uncertainty over the range of a variable and can be used to express the uncertainty in terms of a reliability domain. Using statistical moments associated with a quantity subject to uncertainty is a practical way to quantify the level of uncertainty for a parameter. In particular, the second order moment (i.e., variance) is a measure of the dispersion of a random variable. Either the variance or standard deviation can be used.

Model calibration is also necessary due to the semi-empirical nature of water quality models. However, a calibrated model does not mean that it has predictive capability. It may contain incorrect mechanisms, and the consistency between model simulation results and measured data

could be the result of unrealistic parameter values (Ji, 2008). Calibration is the first stage testing or tuning of a model to a set of data, preferably not used in the original model construction (Thomann, 1982). Calibration or tuning should include consideration of a consistent set of theoretically defensible parameters and inputs.

Model verification is important and can confirm that a calibrated model is useful over an extensive range of conditions in a water body (Ji, 2008). To verify a model, the conditions, such as the range of applicability (physically, chemically, or biologically), should be specified (Thomann, 1982). Any mechanisms, which were identified as a part of the initial construct but not incorporated in the verified model or vice versa, should be summarized. A verified model provides more confidence to predict future conditions of a system (Ji, 2008). However, the verified model is still limited to the range of conditions defined by the data sets used in calibration and verification procedures except if they are extrapolated. Any model prediction outside this range remains uncertain. A good verified model does not imply the ability to accurately predict future or distant water quality (Thomann, 1982).

Calibration and verification of a water quality model are not simply curve-fitting exercises but wherever possible should reflect more fundamental theoretical constructs and parameters (Thomann, 1982). James and Bierman (1995) suggested three ways of model calibration and validation: (i) graphing model output and observed data over time, (ii) Student's *t*-test between mean of model output and mean of field data for a time period (e.g. a year), and (iii) regression analysis of averaged model output (independent variable) with averaged observed data (dependant variable) for a time period (e.g. day or month).

With high performance computers, studies on stochastic processes and uncertainty analysis can be achieved, such as through Monte Carlo simulation (MCS), which is a powerful tool in many fields of mathematics, physics, and engineering (Dimov and McKee, 2007). MCS is a technique that generates random values of stochastic input parameters according to their respective probabilistic characteristics (Tung and Yen, 1993). In MCS the system response of interest is repeatedly measured under various sets of system parameter that were generated from unknown or assumed probabilistic laws (Tung and Yen, 2005). It offers a practical approach to uncertainty analysis because the random behaviour of the system response can be probabilistically duplicated. The general procedure of MCS are: (1) to generate a large number of random sets to compute corresponding model sets, and (2) to analyze simulated model output to determine the statistical characteristics of model output such as the mean, variance, and PDF.

Particularly, the bootstrap resampling method, which is a form of MCS first proposed by Efron (1982) to deal with the variance estimation of sample statistics based on observations, has been applied for uncertainty analysis for several decades (see e.g., Pandey *et al.*, 2003; Tung, 1993; Tung and Mays, 1981 and 1982). Efron (1982) and Efron and Tibshirani (1993) reviewed and summarized bootstrap techniques and their variations. The examples of bootstrap application included quantifying the uncertainty of the parameters of a probability distribution and the sample skewness coefficient in flood frequency analysis (Tung and Mays, 1981) and assessing the uncertainty associated with optimal risk-based hydraulic design of bridges (Tung and Mays, 1982). Tung (1993) also discussed its application for the assessment of the confidence interval of optimal risk-based design parameters. In the bootstrap procedure, a synthetic data set is generated by randomly selecting N observations from an original data set, which is the same size

as the original data set (Richardson and Hollinger, 2005). Each synthetic data set will have different elements from the original one. The method assumes that the synthetic data set has a similar PD to that of the original data set. Tung and Yen (2005) presented a basic algorithm of bootstrap technique in estimating the standard deviation associated with any statistic of interest from a set of sample observations that involves the following steps:

- Step1: For a set of sample observations of size n , that is $\mathbf{x} = \{x_1, x_2, \dots, x_n\}$, assign a probability mass $1/n$ to each observation as Eq. (2.39)

$$\hat{f} : P(X = x_i) = 1/n, \quad i = 1, 2, \dots, n \quad (2.39)$$

Where \hat{f} is the non-parametric maximum likelihood estimator of the unknown probability mass function $f_x(x)$ for each individual observation.

- Step 2: Randomly drawn observations from the original sample set using \hat{f} to form a bootstrap sample, $\mathbf{x}^* = \{x_1^*, x_2^*, \dots, x_n^*\}$. Note that the bootstrap sample \mathbf{x}^* is a subset of the original samples \mathbf{x}
- Step 3: Calculate the value of the sample statistic $\hat{\Theta}_*$ of interest based on the bootstrap sample \mathbf{x}^*
- Step 4: Independently repeat Steps 2 and 3 a number of times M , obtaining bootstrap replication of $\hat{\theta}_* = \{\hat{\theta}_{*1}, \hat{\theta}_{*2}, \dots, \hat{\theta}_{*M}\}$ and calculate by Eq. (2.40)

$$\hat{\sigma}_{\hat{\theta}_*} = \left(\frac{1}{M} \sum_{m=1}^M (\hat{\theta}_{*m} - \hat{\theta}_{*\bullet})^2 \right)^{0.5} \quad (2.40)$$

Where $\hat{\theta}_{*\bullet}$ is the mean of the bootstrap replication of $\hat{\Theta}_*$, which is calculated by Eq. (2.41)

$$\hat{\theta}_{*\bullet} = \frac{1}{M} \sum_{m=1}^M \hat{\theta}_{*m} \quad (2.41)$$

This algorithm is called nonparametric unbalanced bootstrapping. The parametric version of this algorithm can be made by replacing the nonparametric estimator \hat{f} by a parametric distribution, in which the distribution parameters are estimated by the maximum likelihood method. More specifically, if one judges that on the basis of the original data set, the random observations $\mathbf{x} = \{x_1, x_2, \dots, x_n\}$ are from, for instance, a lognormal distribution, then the resampling of x 's from \mathbf{x} using the parametric mechanism would assume that \hat{f} is a lognormal distribution. Fig. 2.2 shows the flowchart for this basic bootstrap algorithm. Similar to Monte Carlo simulation, the accuracy of estimation increases as the number of bootstrap samples gets larger. However, there exists a tradeoff between computation cost and the level of accuracy desired. Efron (1982) suggested that 200 times of bootstrap resamples are generally large enough for estimating the standard deviation, while 1000 times of resamples are needed to estimate the confidence interval with reasonable accuracy.

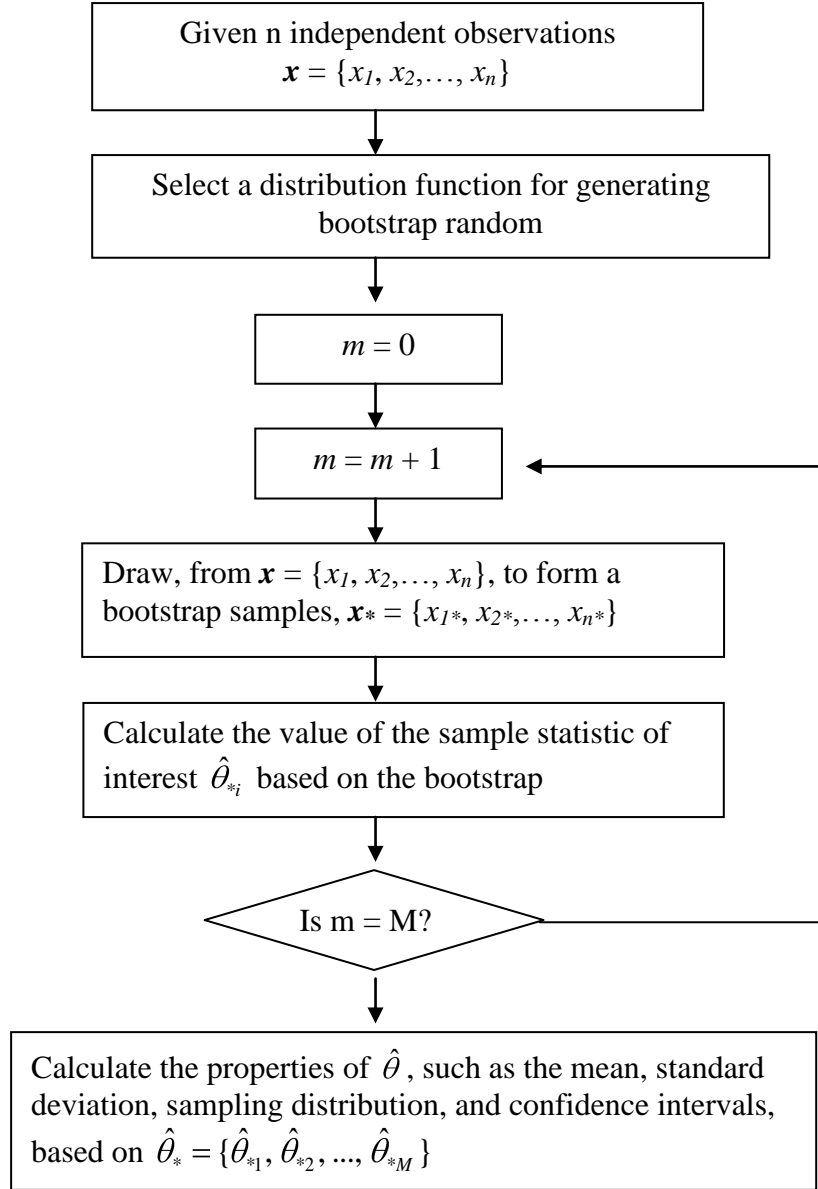


Fig.2.2: Flowchart of basic bootstrap resampling algorithm (source: Tung and Yen, 2005).

2.6 Remarks

Previous studies examined inland spills in different areas in Southern Ontario from various perspectives. They started with spill database analysis to point out the problem of inland spills and then raised their research interests and purpose. However, each study only focused on one

aspect of inland spills - economic damage of oil spills (Tang, 2005), a web-based GIS for inland spill management (Han, 2007), and risk-based spill management criteria (Cheng, 2010). This research is comprehensive in that it includes probabilistic occurrences, fate of spills along rivers, risk analysis of water quality violation in compliance with associated standards at downstream locations along rivers, and management planning framework of inland chemical spills. The following are remarks based on literature review:

- The data analysis results, including spilled time, mass, and NAICS-based location, are used for the development of associated PD models to achieve one of the research objectives – predicting inland chemical spill probabilistic occurrences.
- MCS is applied for simulating the probabilistic occurrences by time, magnitude, and location in a certain area. MATLAB software is used to develop the associated MCS program.
- One thousand times of nonparametric unbalanced bootstrapping is employed to analyze the uncertainties of the PD's parameters and inadequate representation of inland spills data.
- Benzene spills in the St. Clair River AOC are used as case study and their characteristics are further transferred to the Mimico Creek watershed – a hypothetical case study.
- The water quality models SpillMan for the St Clair River and Neely *et al.*'s model (1976) for small rivers will be applied for the case studies to demonstrate the developed MATLAB-based MCS models associated with inland benzene spills, which can achieve another research objective – quantitative risk analysis of water quality impairment at downstream locations along rivers.

CHAPTER 3 INLAND SPILLS IN SOUTH ONTARIO

Chemical spills have been of great concern by the public and politics over the past decades due to extraordinary spill events in southern Ontario. This chapter mainly focuses on the inland chemical spill characteristics in Southern Ontario and their significance. In particular, benzene spills in the St Clair River AOC are analyzed because benzene is toxic and carcinogenic contaminant and was among the top 20 chemical pollutants in the Environment Canada's Priority List for the period of 1987-1997 (Fingas et al., 2000).

3.1 Spill Database

The inland chemical spill records for Southern Ontario were originally provided by the SAC and updated by Ryerson University (e.g. assignment of longitude and latitude of spills, spill locations, etc.). The SAC database records the majority of spill events and other urgent environmental occurrences. Chemical spills as defined by the SAC include releases of acids, bases, solvents, pesticides, other organic and inorganic chemicals, liquid industrial waste, sewage, and liquid hazardous wastes, smoke, dust/particulates, nitrous oxide, natural gas, and others. The major spill attributes in the updated SAC database include date, geo-coding, region/municipality, chemical type, volume/mass (estimated), location, corporation, source, sector, cause and environmental impact. In addition to the updated SAC database, the SLEA provided industrial chemical spills records between 1986 and 2005 in the Sarnia-Lambton Area, some of which had caused WTP shutdowns in the St Clair River AOC (Cheng 2010). In comparison to the SAC database, the major attributes in the SLEA database only include spill date, chemical type, estimated quantity,

discharge classification and shutdown records.

While some spill events are recorded in both databases, there are discrepancies between the two recording systems. This may be attributed to the definition of spill events and differences in the use of spill information between the SAC and the SLEA. The SAC is a provincial agency which collects and coordinates spill response. Its mandate addresses provincial priorities and fulfills the requirements of reporting and cleaning up spills immediately and restoring the environment promptly by the owner of the spilled material, the person causing/permitting the spill, and the person controlling a material when it was spilled under the Environmental Protection Act (Ontario MOE 2007a, 2012). The spill data are analyzed annually to identify spill occurrences and types in various regional municipalities and industries. The SLEA is an industrial association which focuses on local industrial cooperation and sharing of technical information. It is understandable that the data collected by these organizations are not consistent.

3.2 Statistical Characteristics of Chemical Spills in Southern Ontario

As recorded in the SAC database, Southern Ontario experienced 13,682 chemical spills involving more than 1,000 chemicals between 1988 and 2007, resulting in multiple environmental impacts such as air, water and land contamination. The attributes of spill date, quantities, industry, and location are the most important information for this study which investigates the probabilistic occurrences of a certain type of inland chemical spill (mass and time) characterized by the North American Industry Classification System (NAICS)-based locations. Spills from industrial facilities with the same NAICS code are hypothesized to have similar spill properties (e.g. probability distributions of spill occurrence times and spilled mass)

which are used for the risk-based analysis of surface water quality violation caused by chemical spills. In addition to the SAC database, the SLEA industrial spill database recorded 801 chemical spills involving more than 280 chemicals between 1986 and 2005 in the Sarnia-Lambton Area. After the SAC and the SLEA databases are synchronized in terms of spill date, chemical type and region, a total of 14,174 chemical spills were compiled for the regions of Toronto, Hamilton, Peel, Niagara, Lambton, Essex, York, Halton, Durham, Guelph and London between 1988 and 2007. This combined database indicates an annual average of 709 chemical spills, or about two spills per day in Southern Ontario.

The annual occurrences of inland chemical spills together with annual industrial gross domestic product (GDP) for the 1988–2007 period (Statistics Canada 2012) are illustrated in Fig 3.1. While the industrial GDP had grown in this period, the spill occurrences had not shown the same tendency, which may be attributed to the changes in both government policy and industry types from heavy, chemical-based industry to high-tech light industry. For instance, manufacturing has been reported to be struggling for some time in Ontario (CIAC 2012). In particular, the proportion of basic chemicals and resins manufactured in the province (43%) has been declining recently as a result of the closures of aging facilities and little new investment. The region of Sarnia-Lambton is experiencing a new industrial revolution involving the development of new technologies and convergence of others among the chemical, agriculture and automotive sectors (Mallay & McLaughlin 2012). Moreover, the spill trends during the two time periods of 1989–1999 and 2000–2007 are similar (i.e. the number of spills is highest at the beginning of each period and then falls to a lower level in the following years). This may be attributed to the highest industrial GDP growth rates at the beginning of both periods (8.2% in 1989 and 7.8% in

2000) and the slow-down in the following years (Statistics Canada 2012). The Ontario Ministry of the Environment's study also indicated that the number of spills reported to the Ontario SAC and those released from industrial sources increased by approximately 5% and 24%, respectively, between 2003 and 2004 province-wide (Ontario MOE 2005). The return of higher spill occurrences in 2000 may be attributed to a strongly expanding economy between mid-1999 and mid-2000 resulting in a rapid growth of production (Thiessen 2000). Additionally, technical and product innovation and old equipment/machines replacement may have contributed to bringing down the number of spills.

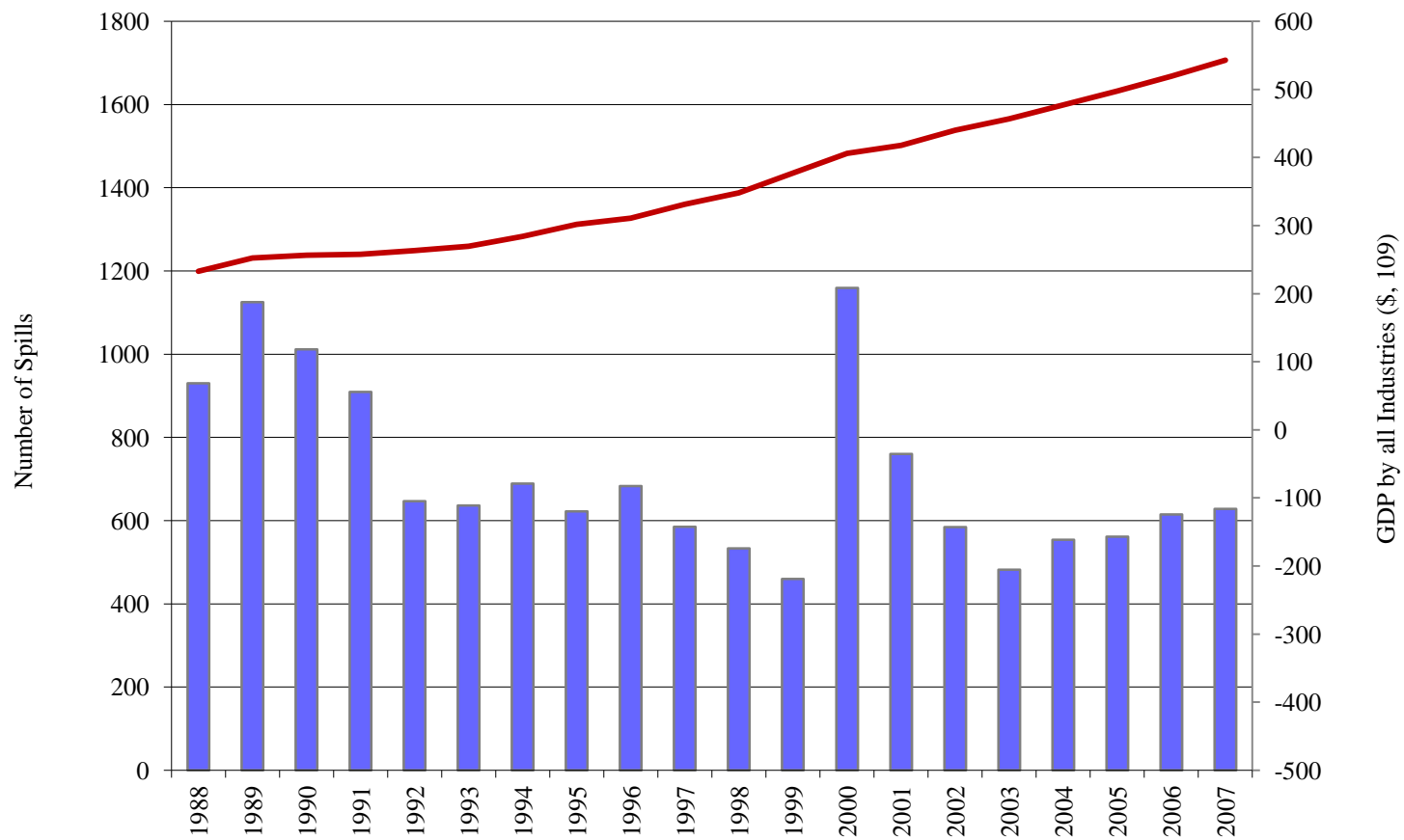


Fig. 3.1: Annual number of chemical spills in Southern Ontario and industrial annual gross domestic product (GDP) at basic prices.

The volume of Ontario imports grew from 1997 to 2007 (Ontario MOF 1995-2011). In particular, the top three international imports, motor vehicles and parts, mechanical equipment and electrical machinery, were related to industries and accounted for over 50% of the total international imports in this period. Moreover, the rapid development of computer technology and industrial automation since 2000 may have played a significant role in reducing the number of spill occurrences in the period 2000–2007. Evidence shows that the Ontario government has provided strong support for research and innovation and this expenditure has increased since 1998 (Ontario MOF 1995-2011). Furthermore, government actions, such as inspection, monitoring, voluntary abatement, compliance, enforcement, penalty and prosecution, are also important impact factors in the reduction of spill occurrences. For instance, the enactment of the Safe Drinking Water Act may be now forcing industries to be more cautious in their plant operation and change their habits. The Ontario Ministry of the Environment Emergency Management Program indicates that ‘a comprehensive emergency management program is one that incorporates a risk management approach supported by the five pillars of emergency management – prevention, mitigation, preparedness, response, and recovery’ (Ontario MOE 2007b). The repeated spill trend in 2000–2007 may reflect the economic fluctuations in Ontario in the past 20 years according to the Ontario economic outlook and fiscal review (Ontario MOF 1995-2011).

The average monthly occurrences of inland chemical spills (1988–2007) together with average monthly temperature (1901–2009) are illustrated in Fig. 3.2. As shown in this figure, the frequency of occurrence of chemical spills is the highest in the month of June (1,442 spills) and the average monthly spill occurrences and average monthly temperature appear to be correlated.

This may be attributed to an increase in transportation activities during summer months (Environment Canada, 2006). Researchers said that “actual changes in temperature, rainfall, and other weather variables have direct effects on various economic series, such as those concerned with agricultural production, construction, and transportation, and consequent indirect effects on other series” (Granger 1978); “weather is a powerful force affecting the economy” (Niemira 2005); and “seasonal fluctuations are an important source of variation in all macroeconomic quantity variables, including consumption, investment, government purchases, employment and the money stock” (Barsky & Miron 1989). Niemira (2005) also raised three basic aspects in assessing weather effects on consumer and business activity: the role of weather as noise in temporarily shifting the timing of purchases or production; the role of weather as a seasonal shock in possibly permanently impacting demand and output; and the potentially casual relationship between weather cycles and macroeconomic activity. He concluded that “weather impacts economic activity”. Consequently, the winter months may result in a total loss of demand and a decrease of production resulting in a small number of spills.

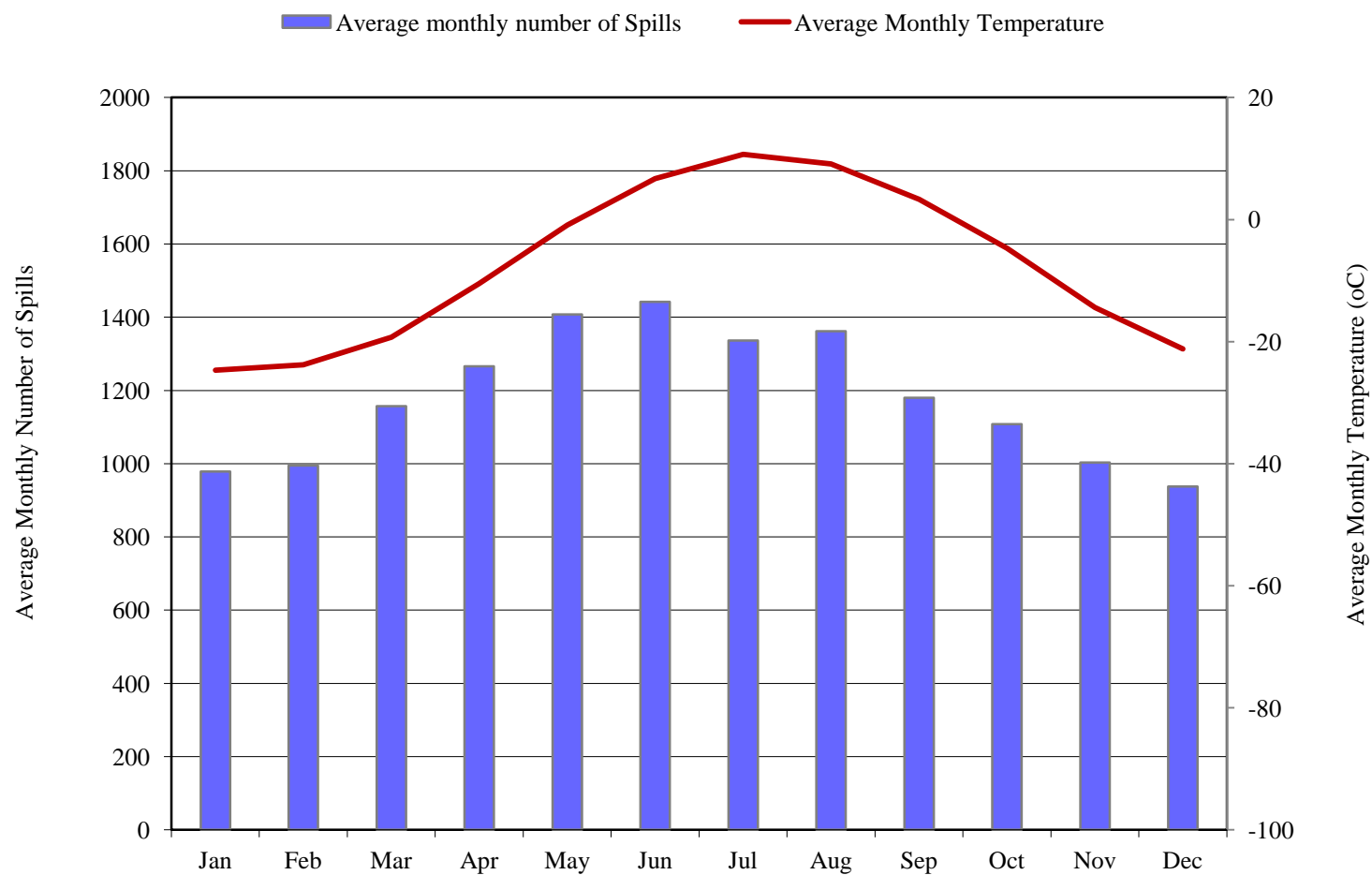


Fig. 3.2: Average monthly occurrence of chemical spills in Southern Ontario (1988–2007) and average monthly temperature in Canada (1901–2009) (The World Bank 2012).

Since the SLEA database does not contain any information on the cause, environmental impact, corporation, and source/sector of spill events, the detailed statistical and spatial analyses of spill characteristics were conducted using the SAC database. Chemical spills occurred in 77 municipalities including Durham, Essex, Guelph, Halton, Hamilton, Lambton, London, Niagara, Peel, Toronto, and York regions of Southern Ontario. The distributions of spills amongst the counties/regional municipalities are shown in Fig. 3.3(a) and (b). Cities/local municipalities such as Toronto, Hamilton, Mississauga, Sarnia and Brampton accounted for 63% of all recorded spills, which may be attributed to the high density of industrial and commercial activities in these cities. Similarly, most chemical spills in the Greater Toronto Area (GTA) were located in the industrial areas of the Cities of Brampton and Mississauga (Li 2005). Approximately 23% and 27% of spills were recorded in 2003 and 2004 at industrial facilities in the City of Sarnia, which has the highest concentration of petrochemical facilities in Southern Ontario (Ontario MOE 2005). These analyses provide very important information to identify potential spill locations and may assist various levels of government in implementing management measures and allocating resources (e.g. finance, human resources, equipment and materials) for spill prevention, control and emergency response.

Twenty-six causes of chemical spills are specified in the SAC database, in addition to instances in which the cause of spills is identified as unknown. Pipe/hose leak, fuel tanks/barrels leak, process upset, discharge/bypass to watercourse, and other discharges are the top five causes recorded, as depicted in Fig. 3.3(c), which contributed more than half of the total number of spills. Other causes shown in this figure include overflow, valve/fitting leak, tank leak and cooling system leak. Moreover, technical limitations, human errors, equipment failure and aged

equipment/machines could be the impact factors causing spill occurrences. These spills could result in surface water pollution, soil contamination, air pollution and multi-media contamination, as shown in Fig. 3.3(d). The spills may also have an impact on human health, vegetation toxicity and result in fish kills, which are included in “Other Impacts” shown in Fig. 3.3(d). About twenty-eight per cent of spills have not anticipated environmental impact, the rest of spills (72%) are specified to have single or multiple environmental impacts. It is observed that the majority of spill impacts are surface water pollution and soil contamination. According to the SAC database, among the total 13,682 chemical spills, about 10% of the spills were cleaned up completely while the remaining spills were either not cleaned up or partially cleaned up. As a result, the environment of Southern Ontario may have been significantly impacted by inland chemical spills from 1988 to 2007. In order to remediate the environmental impacts of chemical spills, spill management measures such as spill preventive maintenance and operation, replacement of aging equipment/machines, improved operation technology and enhanced education and training should be considered in industrial spill management plans.

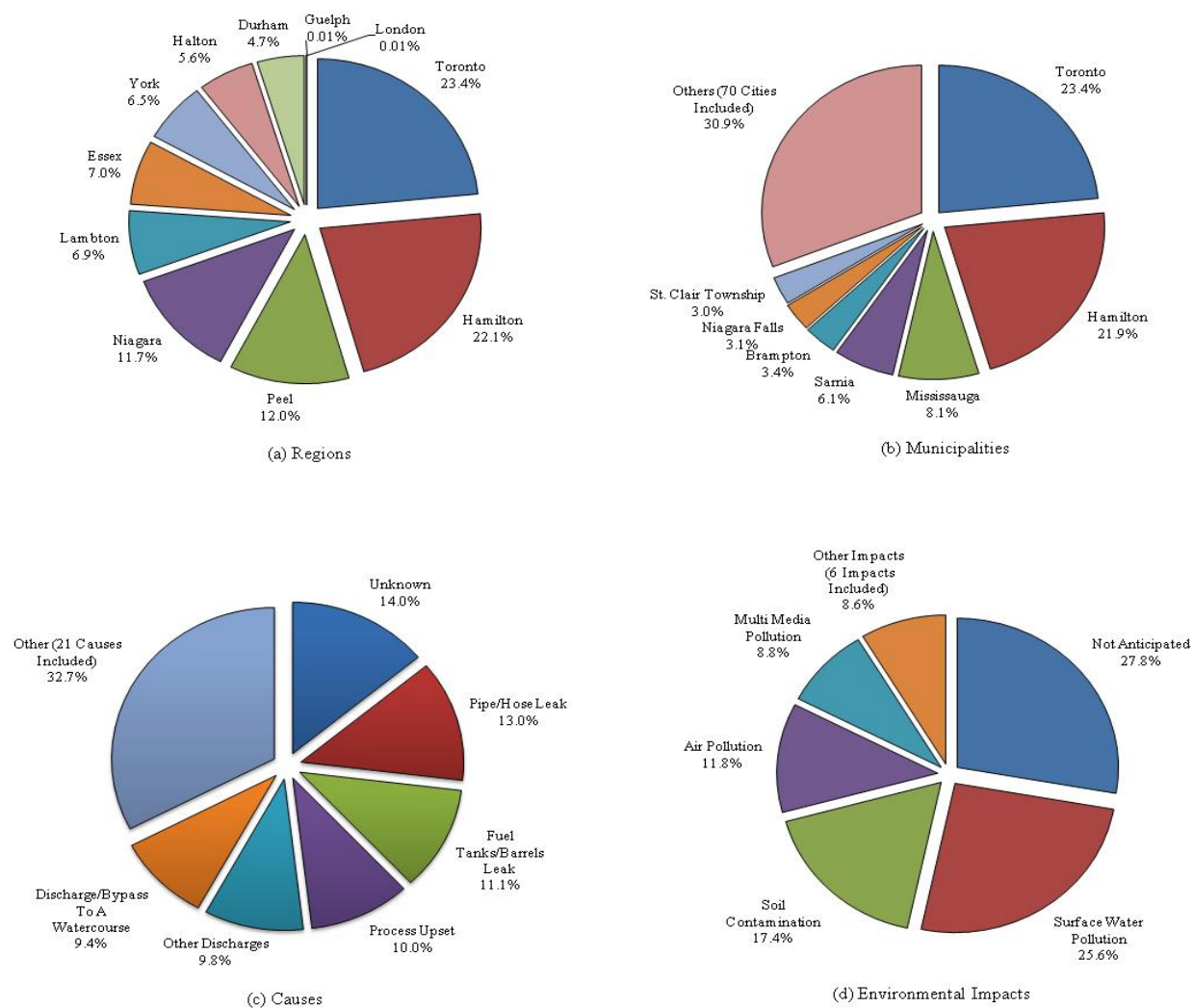


Fig. 3.3: Inland chemical spills in Southern Ontario (based on the SAC, 1988–2007): (a) regions; (b) municipalities; (c) causes; (d) environmental impacts.

3.3 Inland Chemical Spills Leading To Surface Water Impact in Southern Ontario

3.3.1 Statistical Characteristics

The chemical spills which impact surface water (surface-water-impact spills) were compiled from the SAC spill database. As indicated in Table 3.1, there were 4,506 spill occurrences (about 32% of the total chemical spills) involving about 680 chemicals in Southern Ontario in the 1988–2007 period. Amongst them, 1,699 spills had recorded volume and 228 spills had recorded mass. The rest of the spills were identified as unknown quantities. The total volume and mass was about 606 million liters and 634 thousand kilograms, respectively. The annual occurrence of reported chemical spills fluctuated from 57 to 466, while the annual spill volume and mass had wide ranges from about 27,000 to 301 million liters and 46 kg to 262,000 kg, respectively. The average annual occurrence of chemical spills was about 225. Meanwhile, the average annual spill volume and mass was more than 30,000 liters and about 32,000 kg, while the maximum reported spill volume and mass were about 145 million liters (dirty water with sand and suspended solid caused by discharge/bypass to a watercourse from a steel filtration plant) and 200,000 kg (calcium chloride in an overflow from a chemical industry). It is noted that both annual spill volume and annual spill mass have large fluctuations.

In terms of surface water impact, 68 local municipalities in the regions of Durham, Essex, Halton, Hamilton, Lambton, London, Niagara, Peel, Toronto and York in Southern Ontario have experienced chemical spills (see Fig. 3.4(a)). Cities such as Toronto, Hamilton, Mississauga, Sarnia and Brampton have the highest frequency of chemical spill occurrences, as shown in Fig.

3.4(b), which accounted for about 63% of the surface-water-impact spills reported. Compared with Fig. 3.3(b), this observation is similar to that for the total spills, implying that chemical spills may also significantly impact other environmental media such as soil and air in these municipalities.

3.3.2 Spatial Characteristics

The ArcGIS-based spatial distribution of the surface-water-impact spills in all reported municipalities is presented in Fig. 3.5. It is observed that the cities that have higher densities of industries (small dots shown in the figure) have the larger number of surface-water-impact spills in cities, such as Toronto, Hamilton, Mississauga, Sarnia, and Brampton. This might explain the higher proportion (63%) of all recorded surface-water-impact spills in these five cities as mentioned above. It is also noted that the St Clair River and the Humber River are the two major rivers which have received the most spills (i.e. Sarnia and Toronto) and may potentially suffer local water quality impairments, which may be attributed to the fact that 450 petrochemical facilities are located within a 30 km stretch of the St Clair River (Ontario MOE 2005) and 5.6% (5,760 hectares) of the total area of the Humber River watershed has industrial land use (TRCA 2008).

Table 3.1: Annual statistics of chemical spills in Southern Ontario (surface water impact, 1988–2007).

Year	# of total spills	# of spills with volume	Total volume (m ³)	Average volume (m ³)	Max volume (m ³)	Min volume (10 ⁻³ m ³)	# of spills with mass	Total mass (kg)	Average mass (kg)	Max mass (kg)	Min mass (kg)
1988	63	29	156	5	100	1	6	17,244	2,874	9,000	4.5
1989	57	25	4,316	173	3,600	1	3	107	36	78	10
1990	185	90	76,569	851	35,230	0.5	14	23,616	1,687	11,800	5
1991	234	129	24,867	193	7,200	0.1	26	261,526	10,059	200,000	1.5
1992	159	80	24,414	11,555	7,200	0.3	20	65,684	3,284	50,000	1
1993	171	73	301,420	4,129	144,500	2	19	21,204	1,116	13,500	1.3
1994	208	82	1,459	18	300	1	13	20,995	1,615	19,000	1
1995	168	80	15,227	190	6,000	1	7	36,158	5,165	30,000	6
1996	196	79	2,285	29	625	0.5	26	2,438	94	1,000	1.5
1997	175	79	12,471	158	9,166	1	18	7,071	393	2,000	0.5
1998	172	78	3,852	49	1,000	0.1	8	1,076	134	1,000	0.5
1999	176	79	2,440	31	800	1	10	30,165	3,016	13,000	0.5
2000	466	148	20,694	141	5,000	1	14	16,977	1,213	4,000	20
2001	333	110	62,022	564	37,698	1	9	2,157	240	730	1.0×10^{-6}
2002	247	100	18,251	183	14,000	0.3	6	63,141	10,524	30,000	1
2003	252	22	584	27	300	9.1	4	4,933	1,233	3,864	0.9
2004	257	19	27	1	13	45.5	1	46	46	46	46
2005	289	49	1,561	32	918	0.5	3	309	103	236	7
2006	361	181	8,404	46	2,300	0.1	12	50,621	2,862	21,000	1.2
2007	337	167	25,253	150	15,150	0.3	9	8,598	955	5,080	1.4×10^{-2}
Total	4,506	1,699	606,271	18,525	291,100	67.2	228	634,063	46,648	415,334	109.4
Mean	225	85	30,314	926	14,555	3.4	11	31,703	2,332	20,767	5.5
Max	466	181	301,420	11,555	144,500	45.5	26	261,526	10,524	200,000	46
Min	57	19	27	1	13	0.1	1	46	36	46	1.0×10^{-6}
Median	202	80	10,437	146	4,300	1	10	17,110	1,223	7,040	1.2
St. Dev.	98	46	67,006	2,662	32,445	10.1	7	57,842	3,052	44,196	5.5

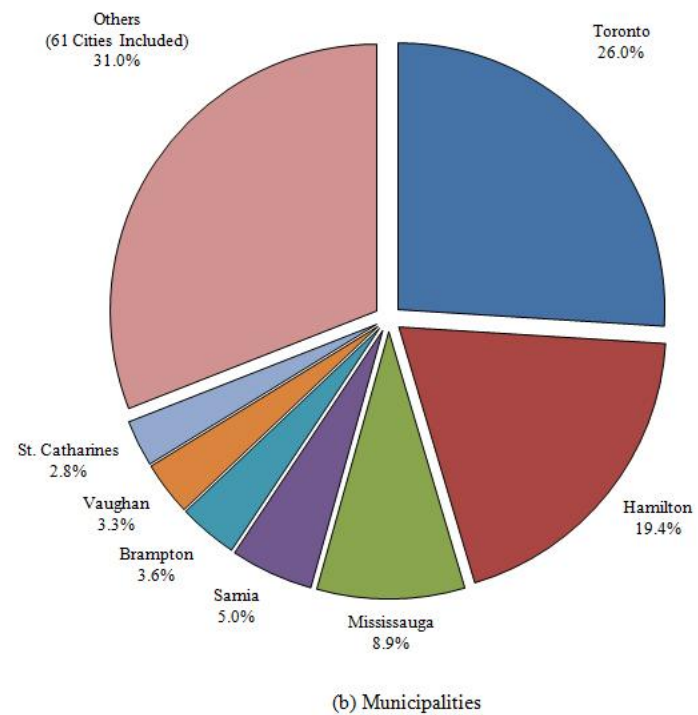
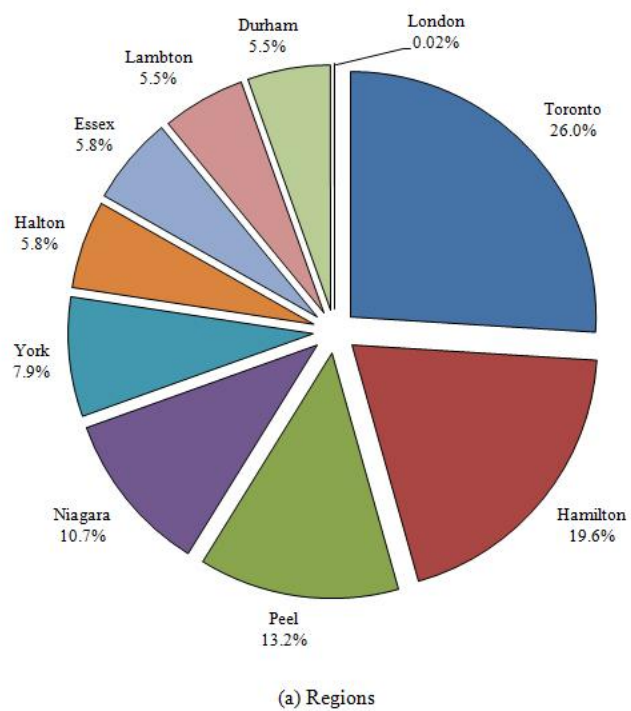


Fig. 3.4: Inland chemical spills impacting surface water in: (a) regions; and (b) municipalities.

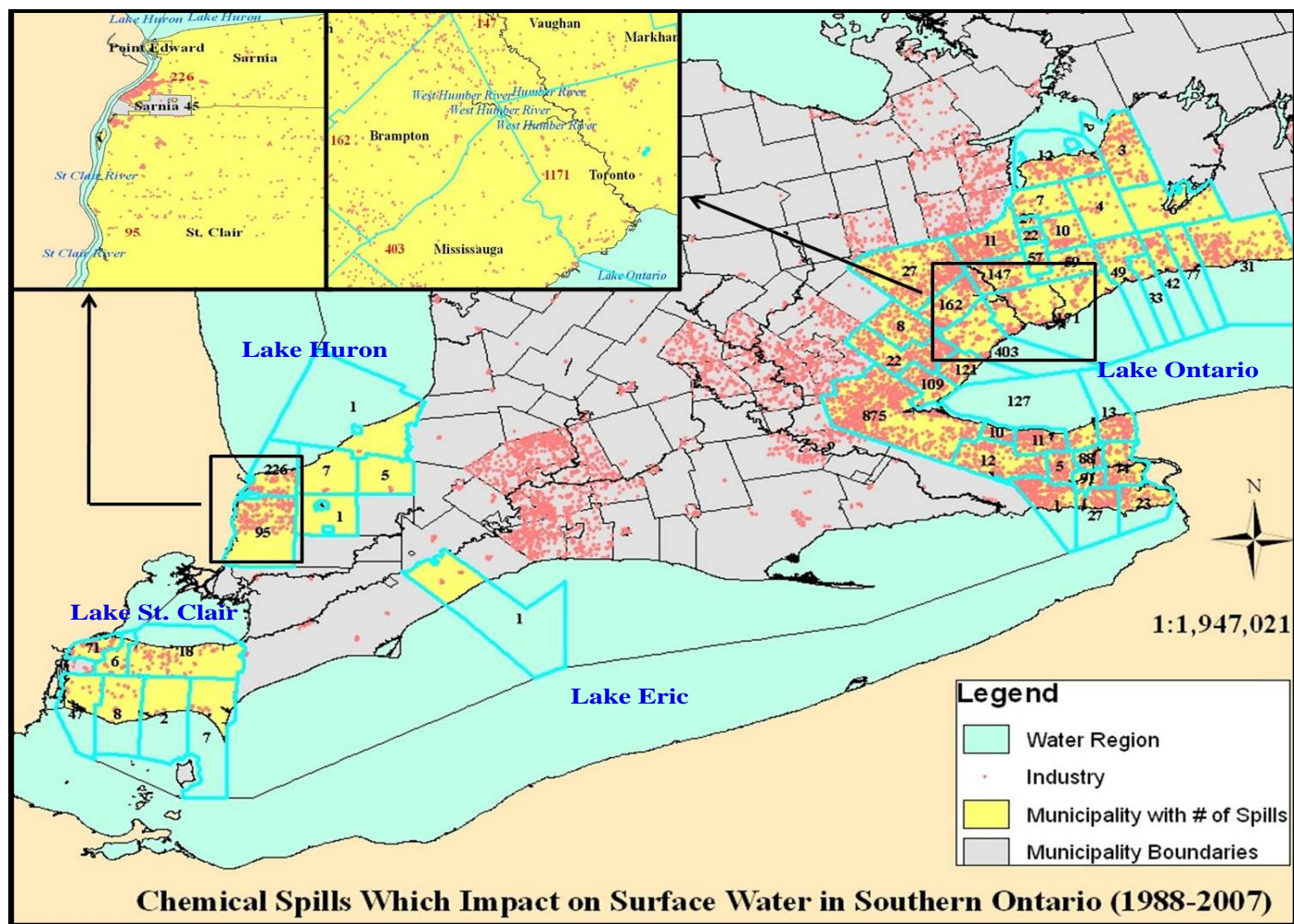


Fig. 3.5: Spatial distribution of inland chemical spills which impact surface water in Southern Ontario (1988–2007).

Among the surface-water-impact spills in Southern Ontario, raw unchlorinated sewage (7.7%), unknown chemicals (4.5%), ethylene glycol (3.7%) and wastewater N.O.S. (2.4%) are the fore most frequent chemical spills. However, dirty water with suspended solids/sand and calcium chloride not only have the largest total volume (301 million liters, 49.7% of total volume) and mass (250,000 kg, 39.4% of total mass) but also have the largest volume (145 million liters) and mass (200,000 kg) from a single spill, respectively. The histogram of the occurrences of chemical spills is depicted in Fig. 3.6. It is noted that 88.7% of spilled chemical types occurred less than 10 times and 38.9% occurred only once while only four spilled chemicals (the four most frequent chemical spills mentioned above) occurred more than 100 times during the past 20 years (1988–2007). The top 5 spilled chemicals are raw unchlorinated sewage, unknown, ethylene glycol (antifreeze), wastewater N.O.S., and blast furnace recirculation water. These results imply that many types of chemicals involved in spill events could lead to complicated and frequent surface water pollution over a wide area and bring difficulties in protecting water resources in Southern Ontario. The large number of spilled chemicals from various industries also implies that a vast number of industries or production lines are involved in chemical spill events in Southern Ontario resulting in water quality deterioration. Therefore, the industries that have frequent spill occurrences and high spill quantities in the past should develop comprehensive spill management plans, which address the use of chemicals in relation to their production processes to prevent spill occurrences and minimize their potential threats to human health and/or the environment in the future. Other industries would also be encouraged to prepare spill management plans for the purpose of spill prevention and emergency response. A comprehensive inland chemical spill management strategy that is developed province-wide jointly by governments and industries could better protect Ontario water resources.

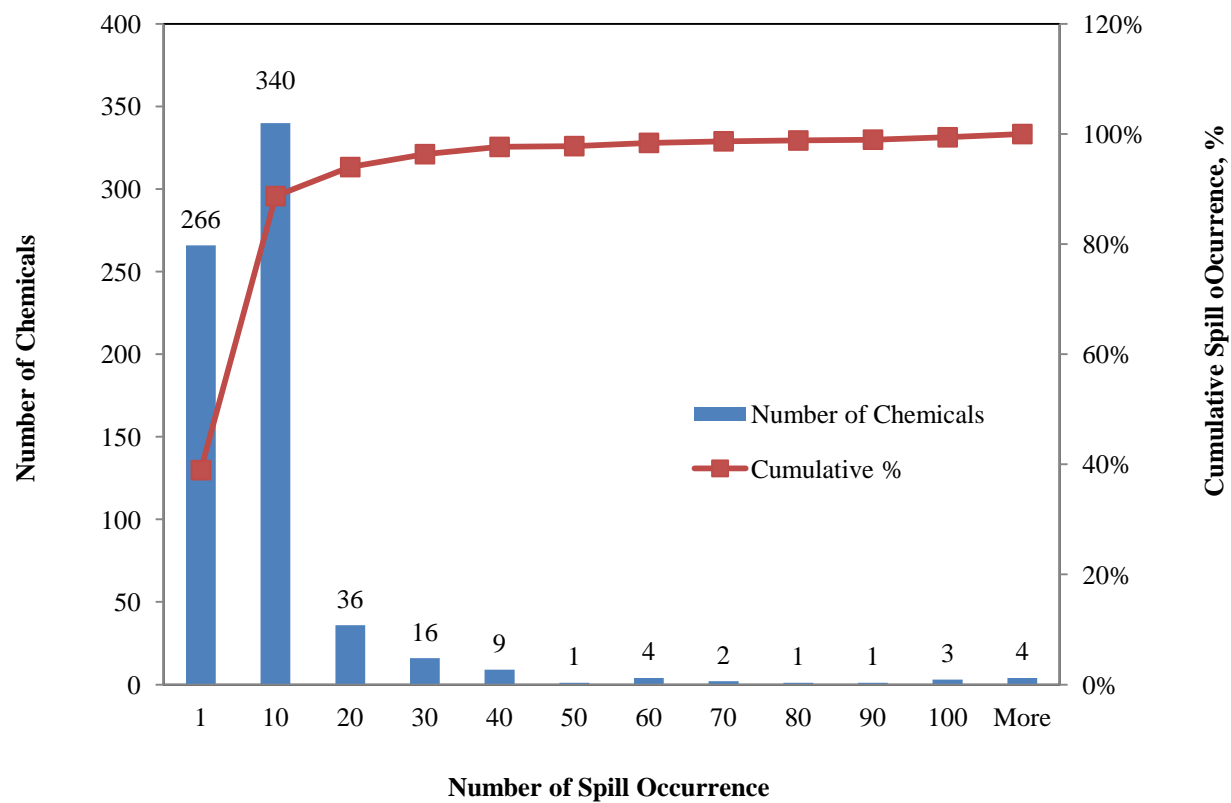


Fig. 3.6: Histogram of the occurrences of chemical spills which were reported to have had surface water impact in Southern Ontario (1988–2007).

The most frequent occurrence of surface-water-impact spills originated from industrial plants (45%) including manufacturing, processing facilities and petroleum refineries, followed by other sources which are not defined (17%), motor vehicles (5%), municipal/industrial wastewater collection system (4%) and sewage treatment plants/lagoons (3%). Unknown sources produce the third largest number of spills (16%). Industrial plants also generated a large portion of spilled chemical volume (about 498 million liters, 82% of total volume) and mass (490,000 kg, 77% of total mass). Local municipalities to a greater extent should develop spill management strategies in which the highly industrialized area in proximity to a surface water body is emphasized. The metallurgy, chemical and general manufacturing sectors have the highest frequency of spills in addition to instances in which the sector responsible for the spills is defined as unknown, as shown in Fig. 3.7. “Other Sectors” shown in this figure include service industries, petroleum, government municipal, food processing, pulp & paper, retail, residential/private, and other. The largest single spill volume and mass are generated from the metallurgy (478 million liters, 79% of total volume) and chemical sectors (375,000 kg, 9% of total mass). These analyses could assist both government and industries to effectively allocate resources to prevent and minimize spill occurrences which impact on the environment.

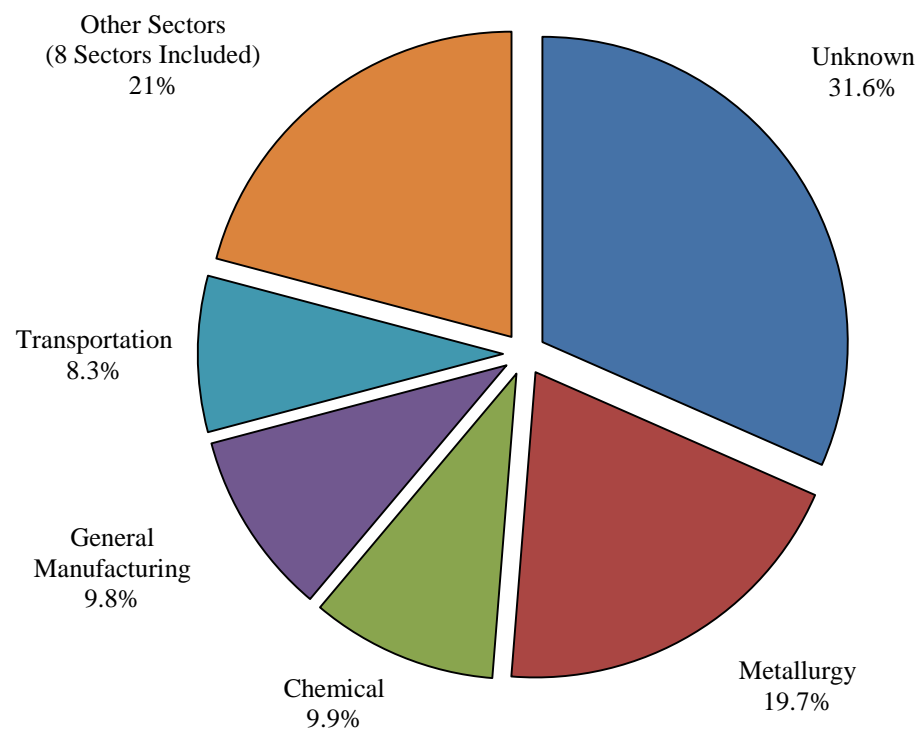


Fig. 3.7: Distribution of chemical spills by sectors which were reported to have had surface water impact in Southern Ontario (1988–2007).

In terms of the causes of surface-water-impact spills, 23 causes including unknown were specified. Some of them had estimated reported volume, others had reported mass, while a majority had no reported volume or mass. Other than the chemical spills with unknown causes, the cause ‘discharge/bypass to watercourse’ is the most frequent followed by causes such as ‘other discharges’, ‘container/tank/lagoon overflow’ and ‘pipe/hose leak’. The total occurrences, total volume and mass of chemical spills are presented in Table 3.2. It is observed that the occurrences of these five causes account for 80% of the total but occupy about 96 and 85% of the total volume and mass, respectively. This result may be able to guide not only municipalities but also industries on reporting procedure and the identification of priorities for chemical spill prevention, control and emergency response.

Table 3.2: Occurrence, volume and mass of chemical spills by causes (surface water impact, 1988–2007).

Course	Occurrence	% of total occurrence	Occurrence with volume	Occurrence with mass	Occurrence without quantity	Volume (m ³)	% of total volume	Mass (kg)	% of total mass
Discharge/bypass to watercourse	962	21.3	289	40	633	380,253	62.7	68,262	10.8
Unknown	924	20.5	244	25	655	19,585	3.2	30,693	4.8
Other discharges	493	10.9	169	22	302	11,552	1.9	33,250	5.2
Overflow (containers, tanks, lagoons)	465	10.3	217	27	221	153,844	25.4	256,665	40.5
Pipe/hose leak	450	10.0	210	28	212	8,650	1.4	111,266	17.5
Container (fuel tanks, barrels) leak	324	7.2	249	36	39	5,501	0.9	35,376	5.6
Total	3,618	80.3	1,378	178	2,062	579,385	95.6	535,511	84.5

3.3.3 Benzene Spill in the St Clair River AOC

Benzene is a colorless, sweet smelling, flammable organic chemical liquid with the molecular formula C_6H_6 (Benzene MSDS). Its density varies with temperature (0.8787 kg L^{-1} at 15°C (Benzene MSDS) and 0.8765 kg L^{-1} at 20°C (Lide, 2007)). The solubility in water is 1.8 g L^{-1} at 15°C (Arnold et al., 1958). Benzene is also a confirmed carcinogen for humans (Benzene MSDS). It is toxic to blood, bone marrow, the central nervous system, and the haematopoietic system (at low concentration); it may also damage the liver and urinary system and cause a continuum of haematological changes such as leukaemia (Benzene MSDS; WHO, 2003). Benzene can be used in a number of products such as paint, rubber, detergents, tires, shoes, drugs, plastics, synthetic rubber, phenol, nylon, aniline, polyester resins, dyes, and insecticides (U.S. EPA, 2009a), which implies that a number of industries related to the production and use of benzene could be potential spill sources that may consequently have an adverse affect on human health. Therefore, benzene spills have been of great concern for the local government of the River AOC (Cheng, 2010). In addition, Environment Canada's top Priority List, based on chemical spill data over a 10-year period from 1987 to 1997, show that benzene was among the top 20 chemical pollutants (Fingas et al., 2000).

This research used benzene spills in the St Clair River AOC as a case study to demonstrate the models that were developed for its probabilistic occurrences and risk analysis for water quality violation at the water treatment plant intakes along the river. Therefore, the statistical and spatial characteristics of benzene spills in the St Clair River AOC are mainly focused on in the following sections.

3.3.3.1 Statistical Characteristics

The statistical characteristics of benzene spills in the River AOC were analyzed based on the spill data collected by the SAC and the SLEA between 1988 and 2007. From the 64 benzene spills whose occurrence was recorded in the River AOC, only two occurred in the same day at different workshops of the same industry, and 39 had reported the magnitude of the spill by mass or volume. Industrial plants and pipeline systems in the chemical, general manufacturing, and petroleum refinery sector were the sources of the benzene spills, in addition to unknown/unspecified sectors. In order to determine the probability distribution of benzene spills in the NAICS based group, the spill inter-event time and the spilled mass, as well as simulate the probabilistic spill occurrences in the St Claire River AOC, the two spills which occurred in the same day were treated as one spill. Since temperature was unavailable for correction, spills with magnitudes quantified spills were compiled and the relevant volumes were converted into masses using a density of 0.8765 kg L^{-1} at 20°C (Lide, 2007).

After conversion, the total amount of benzene spills from 1988-2007 is estimated to be approximately 2218 kg (average 111 kg yr^{-1}). The frequency of benzene spills per year quantifiable or not in the River AOC is compared in Fig. 3.8. It is observed that the annual number of benzene spills in the River AOC fluctuated from 0 to 17. Fig. 3.9 presents the environmental impacts (a) and the causes (b) of all benzene spills in the River AOC. It was found that 38% of spills resulted in surface water pollution directly and 38% of them were not identified. Thirty-eight percent of spills were caused by various leaks, such as container leaks, pipe line leaks, and valve/fitting leaks, 24% of them were caused by discharge/bypass to watercourses, and 20% were of unknown causes. About 39% of recorded spills had no accurate

quantities, which may be attributed to the difficulty in estimating the amount of spilled benzene discharging into a watercourse or leaking into the ground. It is expected that some of these frequencies may provide information for associated industries to develop effective spill prevention and control plans at source (e.g. staff training, equipment replacement, operation and maintenance, implemented to prevent and control spills over a realistic period of time).

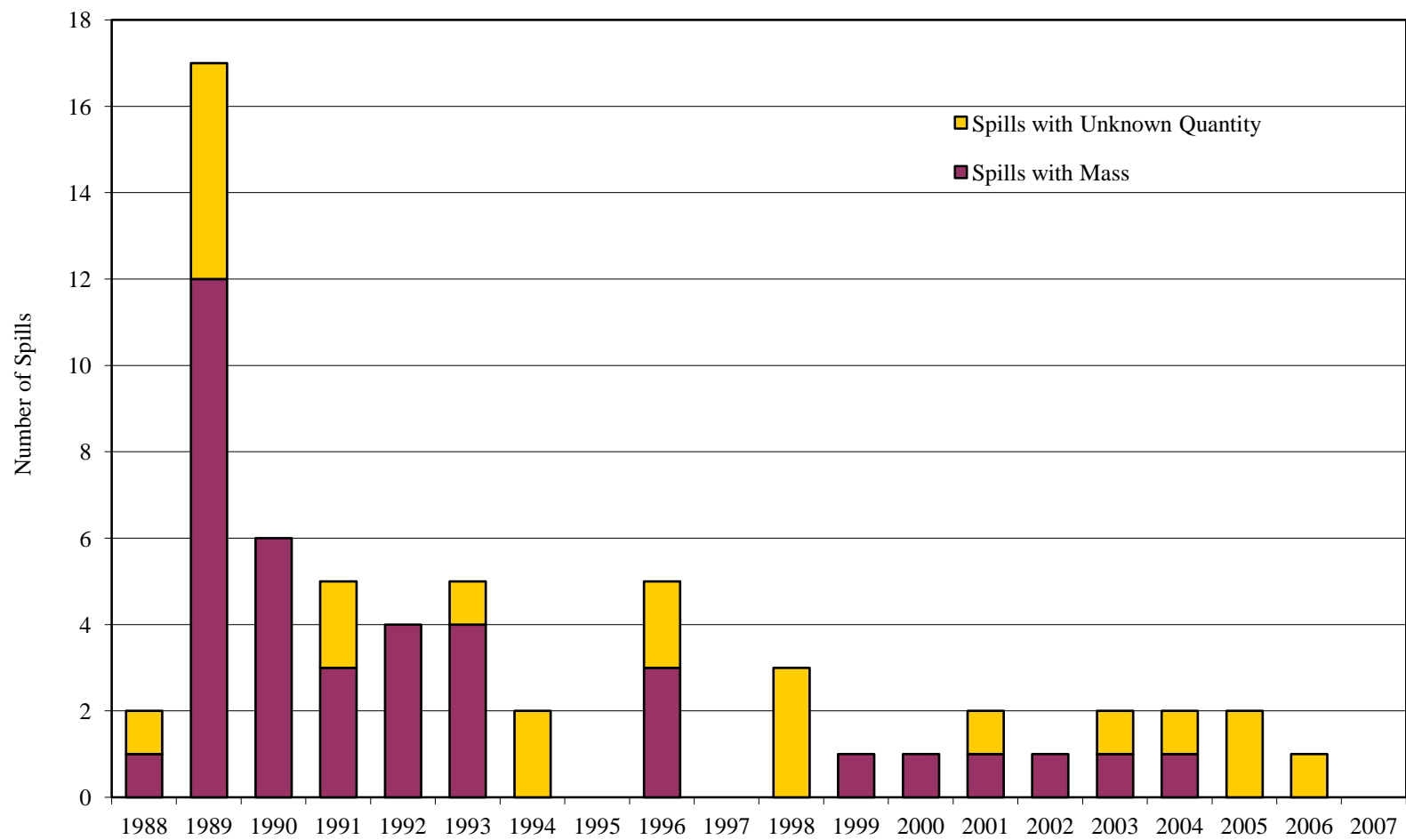


Fig. 3.8: Annual number of benzene spills in the St. Clair River AOC (1988-2007).

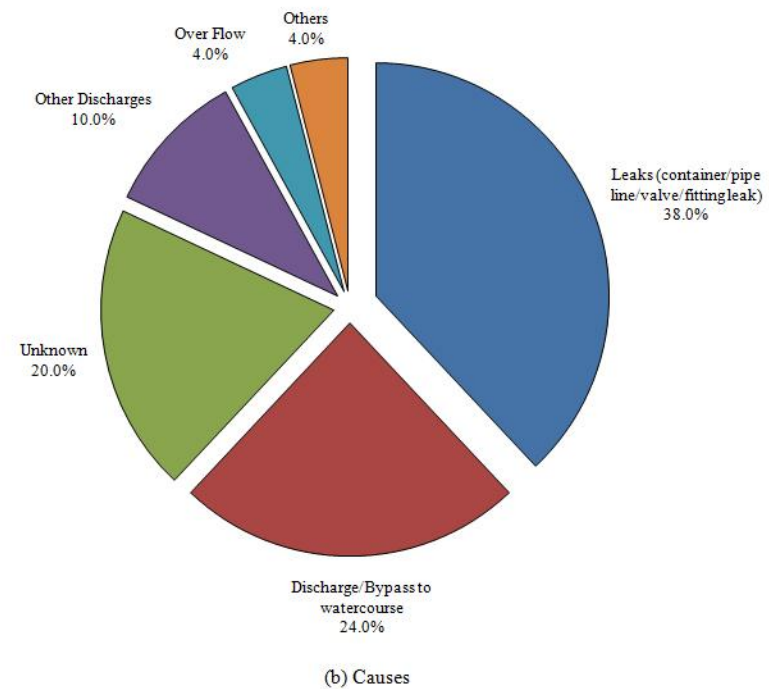
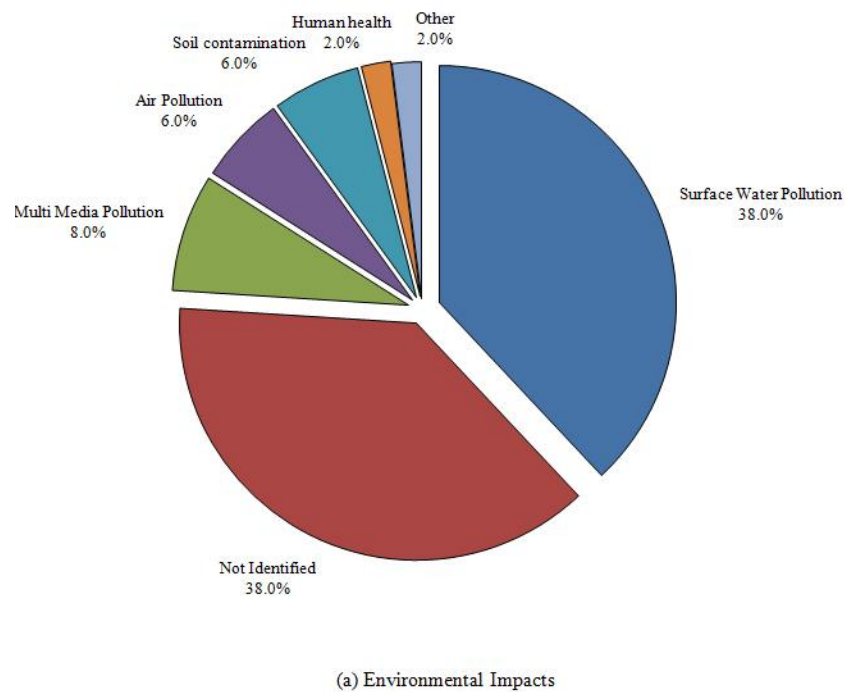


Fig. 3.9: Benzene spills in the St. Clair River AOC (1988-2007).

3.3.3.2 Spatial Characteristics

Under the NAICS, three types of industries, coded as NAICSs 325210, 325110, and 324110, which represent resin and synthetic rubber manufacturing, petrochemical manufacturing, and petroleum refineries are identified to have produced benzene spills in the River AOC, in addition to unknown sources (with the representation of NAICS Unknown). Therefore, a spill's source (a location) can be represented by a NAICS code. The statistics of 38 benzene spills that had magnitudes and formed 3 NAICS based industrial groups (hereafter referred as NAICS groups) along with an unknown NAICS group are shown in Table 3.3. According to the SAC and SLEA databases in the St Clair River AOC, the annual spilled mass varies between 0 to 769 kg, and the mass of the most benzene spills is less than 120 kg, with the exception of two large spills that occurred on March 3rd, 1990 (696 kg, in the group of NAICS 325210) and Jan 21st, 1992 (648 kg, in the group of 324110). The former was caused by fuel tank/barrel leaks from a chemical factory with no anticipated environmental impact, while the latter was caused by a petroleum refinery for unknown reasons resulting in surface water pollution and leading to the shutdown of a water treatment plant (WTP) as recorded in the SLEA database. A spill with a very small mass but with a concentration in violation of benzene's Maximum Allowable Concentration (MAC) in drinking water was recorded to have occurred on July 20th, 1989 (0.0015 kg/45700 litres, also in the group of 324110). Fig. 3.10 illustrates the spatial characteristics of the benzene spills produced by the 3 known NAICS groups, in addition to 11 WTP intakes along the River. The source of each benzene spill of NAICS unknown group is assumed to be any one of the known sources. The spatial analysis provides the information on benzene spill locations in the River AOC and facilitates water pollution transport analysis near a WTP.

Table 3.3: Statistics of benzene spills by NAICS groups in the St. Clair River AOC (1988-2007).

NAICS Group		325210	325110	324110	Unknown
# of Industry Involved		4	2	5	11 *
# of Benzene Spills		12	6	8	12
Spill Event Mass (kg)	Total	1186	123	756	154
	Max	696	79	648	37
	Min	1	1	0.02	1
	Median	42.5	7.9	4.1	6.5
	Mean	98.8	20.4	94.4	12.8
	St. Dev. **	192.4	29.5	225.2	12.2
	90 th Percentile	118.2	50.4	249.2	29.3
Spill Event Occurrence Time (day)	Max	2924	2108	5542	6147
	Mean	1206	1327	1833	2815
	Min	246	855	567	580
	St. Dev.	855	500	1902	2037

Notes: * It is assumed to be all of the industries involved. ** Standard Deviation.

Notes:

1. NAICS 325210 represents Resin and Synthetic Rubber Manufacturing.
2. NAICS 325110 represents Petrochemical Manufacturing.
3. NAICS 324110 represents Petroleum Refineries.
4. It is assumed to be all of the industries involved.
5. St. Dev. is standard deviation.
6. The time series started from Jan 1st, 1988 and end on Dec 31st, 2007.



Fig. 3.10: Spatial characteristics of benzene spills by NAICS codes and the water treatment plant intakes along the St. Clair River.

3.4 Summary of Findings

According to the above statistical and spatial characteristics analysis of the SAC and the SLEA spill databases, inland chemical spills in Southern Ontario from 1988-2007 were continuous non-point pollutants, which had caused impacts on the environment and human health. The other findings are concluded as below:

- Many of inland chemical spills which caused surface water pollution originated from industrial plants. The top four sectors having the most frequent spills include the sectors metallurgy, chemical, general manufacturing, and transportation.
- Major causes of inland chemical spills are pipe/hose leak, fuel tanks/barrels leak, process upset, and discharge/bypass to watercourse, resulting in surface water pollution, soil contamination, air pollution, and other impacts.
- The St. Clair River and the Humber River are the two major rivers which have been exposed to frequent chemical spills resulting in high potential impairments of water/drinking water quality.
- Discharge/bypass to watercourses, other discharges, container/tank/lagoon overflow, pipe/hose leakage, and fuel tanks/barrel leakage are the major causes of chemical spills.
- The majority of spilled chemicals were not cleaned up and their fates in the environment may impact on air, water, and soil quality and human health.
- Benzene spills have been recorded to cause water quality impact and other environmental impacts on the St Clair River.

CHAPTER 4 PROBABILISTIC OCCURRENCE MODEL OF INLAND CHEMICAL SPILLS

Inland chemical spills pose great threats to water quality in worldwide area. A sophisticated probabilistic spill-event model that characterizes temporal and spatial randomness and quantifies statistical uncertainty due to limited spill data is proposed as a major component in spill management and associated risk-informed decision making. It can also help the government for the evaluation of Priority List of spilled chemicals. This chapter describes a MATLAB-based Monte Carlo Simulation (MMCS) model for simulating the probabilistic quantifiable occurrences of inland chemical spills by time, magnitude, and location in a certain area. The NAICS 2012 is used to identify an industry category, which is associated with potential spill locations (i.e. NACIS-based locations) and potential producers in the area. Benzene spills in the St. Clair River Area of Concern (AOC) and the Mimico Creek watershed (hypothetical case) are used as case studies to demonstrate the MMCS model. The probabilistic spill occurrence model is shown in Fig. 4.1.

4.1. Methodology for Probabilistic Simulation of Inland Chemical Spill Occurrences

In designing a stochastic process, inter-event time is a very significant parameter. The cumulative effects of consecutive spills in a short time period are of high concern. After examining the updated SAC and SLEA databases, it was observed that similar chemical spills

rarely occurred more than once on any given day between 1988 and 2007. However, there were close occurrences which might lead to cumulative effects on surface water quality. Additional research on cumulative impact assessment is required but is beyond the scope of this study. The MATLAB-based Monte Carlo Simulation (MMCS) model was developed by assuming that spill occurrence is a homogenous stochastic process and no occurrences happen simultaneously on the same day.

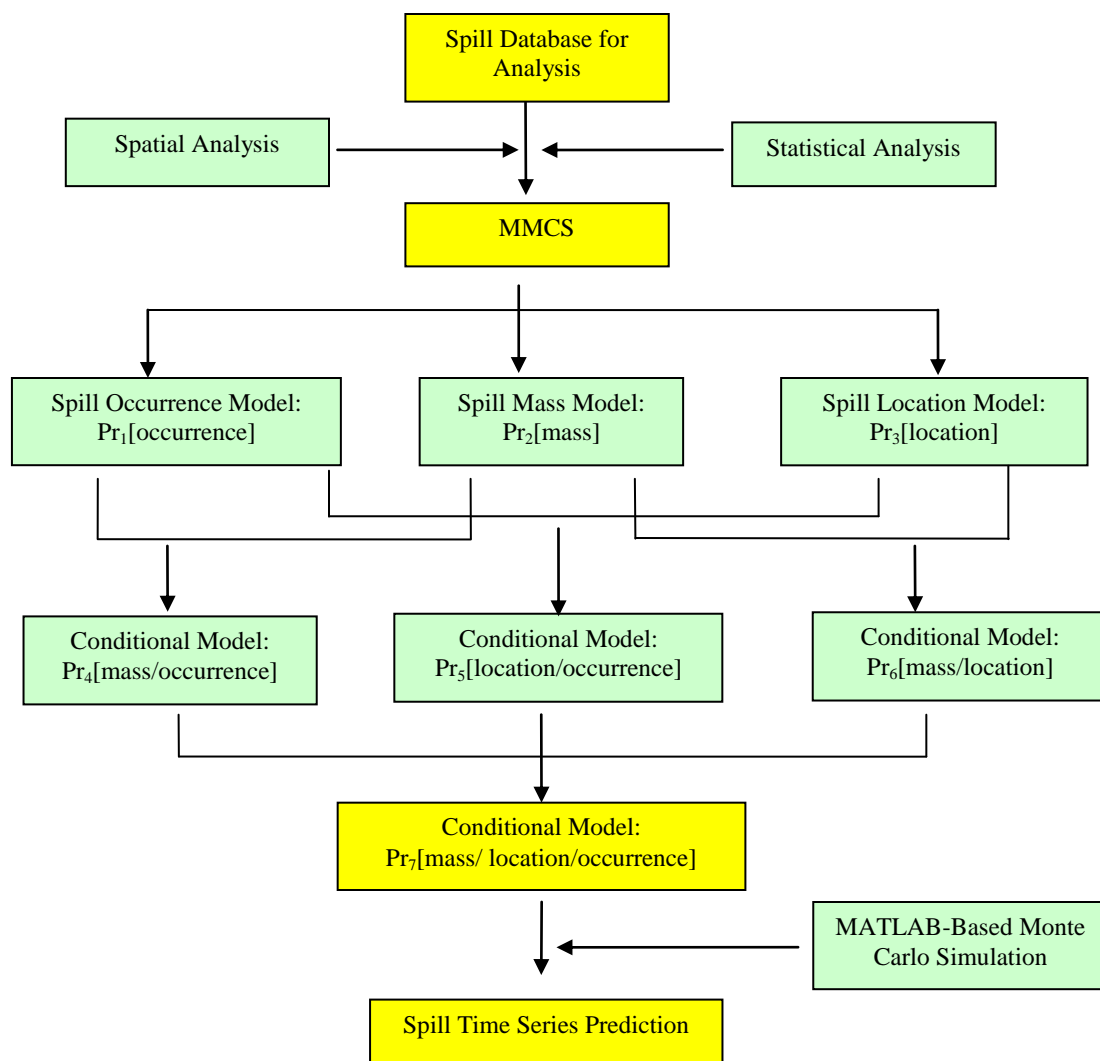


Fig. 4.1: Probabilistic spill occurrence models.

The MMCS model that simulates the probabilistic quantifiable occurrences of inland chemical spills by time, magnitude, and NAICS code location is depicted in Fig. 4.2. The correlations among variables characterizing spills are examined for variable correlativity. Through statistical analysis of historical spill data, the probability distributions (PDs) and their parameters of NAICS code, spill inter-event time, and spilled mass can be determined by the maximum likelihood method. The resulting PDs are applied to generate random variables (i.e. a NAICS code for an industry – a spill location, a spill inter-event time, and a spilled mass). By using the MMCS model, the statistics, such as mean, standard deviation, skewness coefficient and Confidence Interval for each NAICS code can be determined. The uncertainties can arise from (1) determination of the PD and parameters (inter-event time and spilled mass) for each NAICS code, and (2) spill database limitations, including the estimated errors of spill quantity, inconsistency and non-homogeneity of spill data, errors of spill data handling and transcription, and inadequate representation of data due to time and space limitations. This study addresses uncertainties related to model selection and relevant parameters. Other uncertainties, such as spill data uncertainty and human error, are outside the area of this study and have not been analyzed.

The nonparametric unbalanced bootstrapping technique is used in this study to analyze the uncertainties of the PD parameters and inadequate number of spill events. It can substitute sensitivity analysis to investigate parameter uncertainties in the MMCS model. The resampling is done by randomly selecting a synthetic data set following the bootstrap procedure discussed in the Sectin 2.5. The synthetic data is assumed to have the same PD as the original data set and its PD parameters are then estimated using the maximum likelihood method. This procedure is repeated 1000 resamples to estimate a confidence interval and to achieve uncertainty analysis.

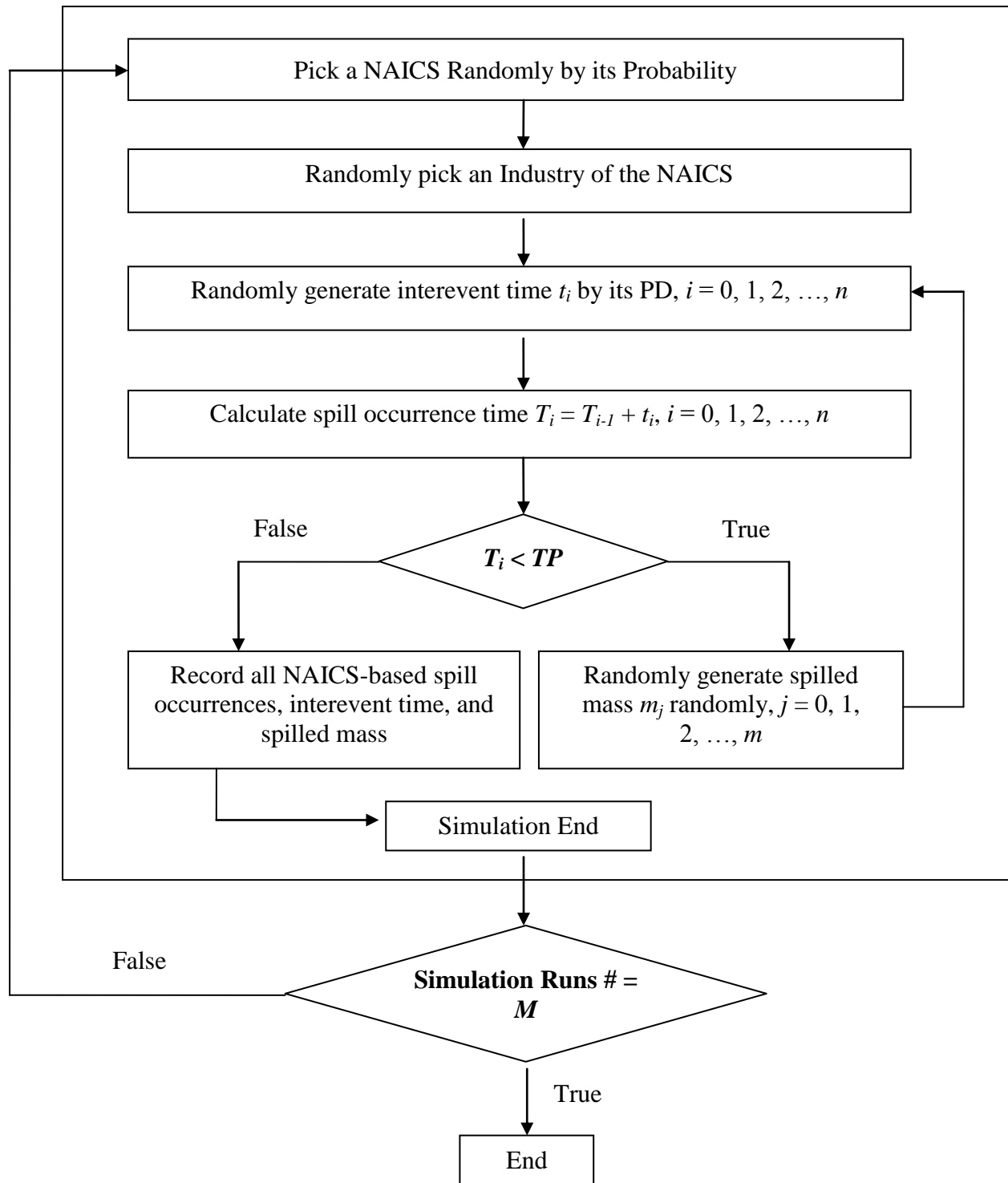


Fig. 4.2: MATLAB based Monte Carlo simulation model for simulating probabilistic occurrences of inland chemical spills in a certain area (M and TP represent the numbers of simulation runs and simulation time period, respectively).

4.2. Case Study: Probabilistic Quantifiable Occurrences of Benzene Spills

With respect to unknown or expected risk to public health, the U.S. EPA National Primary Drinking Water Regulations set out a zero Maximum Contaminant Level Goal (MCLG) and a 0.005 mg L^{-1} Maximum Contaminant Level for benzene concentration in drinking water (U.S. EPA, 2009b). The Guidelines for Canadian Drinking Water Quality and the Ontario Drinking Water Quality Standards set out a 0.005 mg L^{-1} Maximum Acceptable Concentration (MAC) for benzene in drinking water, while the Provincial Water Quality Objectives regulate 0.1 mg L^{-1} as an interim objective for water quality (Health Canada, 1996 and 2010; Ontario MOE, 2002; Ontario MOEE, 1994). The implication is that drinking water quality and human health would be harmed by benzene if its concentration exceeds these regulations/standards.

4.2.1. Correlations of Benzene Spill Data in the St. Clair River

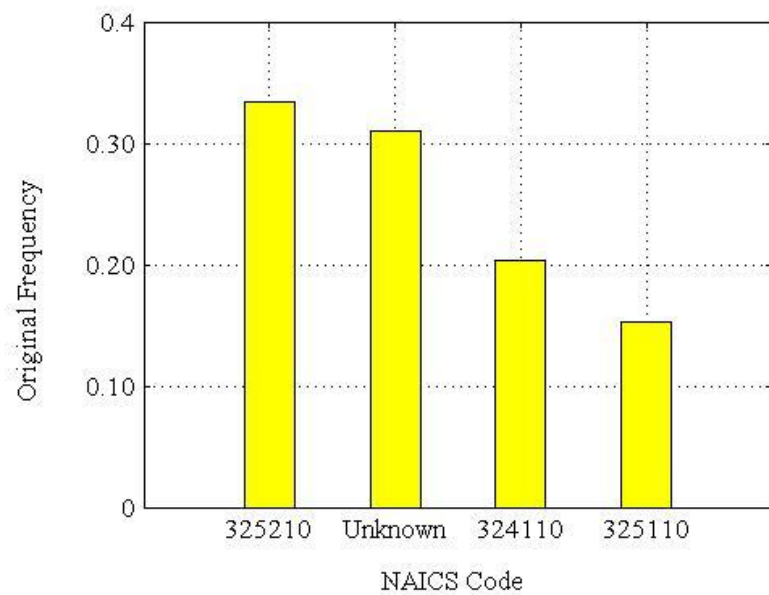
Correlation is one of the most common and useful statistical methods that measures the relation between two or more random variables or two or more sets of data. Since the MMCS model contains 3 variables (i.e. NAICS code, spill inter-event time, and spilled mass) and spill inter-event time comes from spill occurrence time, it is necessary to examine their correlations before applying the model to predict spill probabilistic occurrences. This chapter investigates the correlations between benzene spill inter-event time and spilled mass, and between spill occurrence time and spilled mass. Using regression analysis, very low coefficients of determination (R^2) of 0.014 and 0.025 are obtained for these two cases respectively. Therefore, the investigation concludes in both cases that the investigated variables are virtually independent. It could be assumed that there is no relationship among the industries for benzene spills. The

frequency of NAICS code, spill inter-event time, and spilled mass are also assumed to be independent of each other.

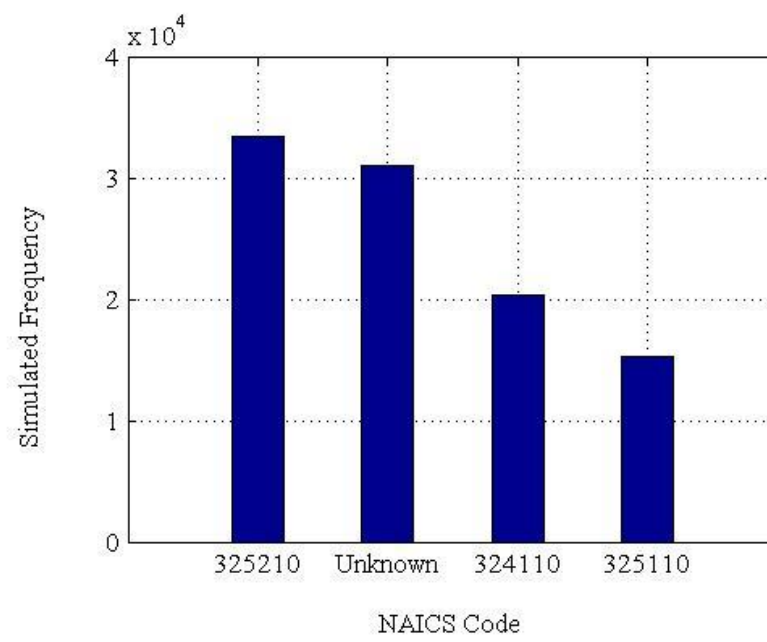
4.2.2. Probability Distributions of Benzene Spill Variables

To simulate the probabilistic occurrences of benzene spills in the River AOC, the probability distributions of spill variables (i.e. NAICS code, spill inter-event time, and spilled mass) were investigated. Using data presented in Table 3.3, the frequencies of spill variables for the 4 NAICS groups were determined. The histogram of NAICS codes is shown in Fig. 4.3 (a). Each NAICS group consists of various industries which are assumed to be equally likely to produce a benzene spill. The frequencies of NAICS groups are assumed to be their probabilities. Therefore, the probability distribution of NAICS groups is treated as a discrete uniform distribution.

The study tested various common used distributions, including normal, lognormal, Weibull, exponential, and Gamma, using the method of maximum likelihood in MATLAB software, to investigate the PDs of the benzene spill inter-event time and spilled mass. The fitted cumulative distribution functions (CDF) using these distributions for benzene spill inter-event time and spilled mass are shown in Fig. 4.4 (a) and (b) respectively. According to the maximum likelihood method, benzene spill inter-event time and spilled mass were better fitted with Weibull and lognormal distributions (solid red lines in the figure), so were those for each NAICS code. Through MATLAB functions “WBLFIT” and “LOGNFIT”, which also apply the maximum likelihood method, the parameters of Weibull (λ and β) and lognormal (μ_y and σ_y) distributions of benzene spill inter-event time and spilled mass respectively, were determined for each NAICS code as summarized in Table 4.1.



(a)



(b)

Fig. 4.3: (a) Histogram of NAICS codes and (b) frequency of simulated NAICS codes of benzene spills in the St Clair River AOC.

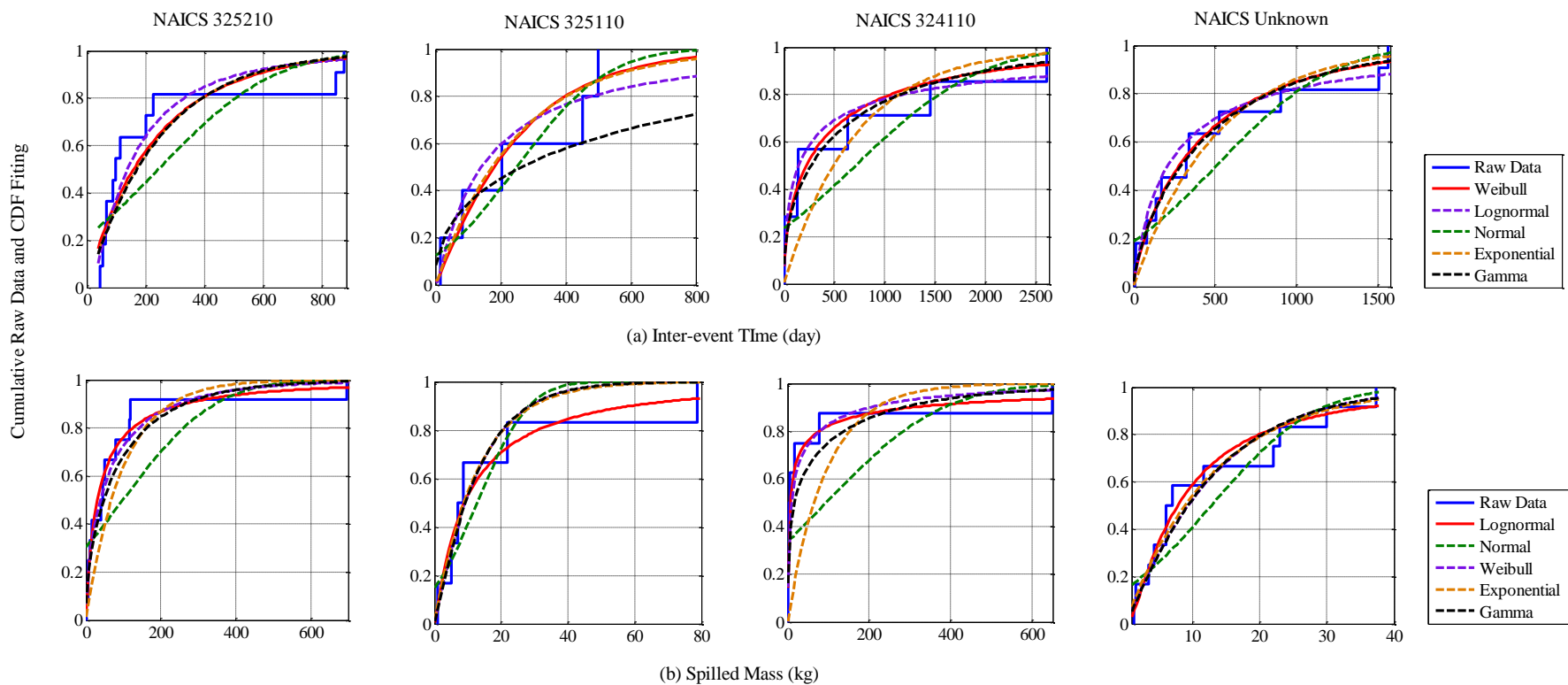


Fig. 4.4: (a) Cumulative benzene spill inter-event time and fitted CDFs and (b) cumulative benzene spilled mass and fitted CDFs of NAICS groups.

Table 4.1: Estimated parameters of the Weibull distribution of benzene spill inter-event time and the lognormal distribution of spilled mass by the MATLAB functions.

NAICS Group	Weibull parameters		Lognormal parameters	
	λ	β	μ_y	σ_y
325210	234.9273	0.9375	3.4156	1.6797
325110	256.0200	1.0634	2.1969	1.4657
324110	435.2951	0.5359	1.7123	3.1279
Unknown	444.8058	0.7852	2.0542	1.1144

4.2.3. Simulation of Probabilistic Occurrences of Benzene Spills in the St Clair River AOC

4.2.3.1. Selection of Simulation Runs and Time Period

The simulation of probabilistic benzene spill occurrences in the River AOC was conducted following the procedure shown in Fig. 4.1. The MATLAB functions “RAND”, “RANDINT”, and “LOGNRND” were used to generate random variables of NAICS code, an industry from NAICS group, and spilled mass, respectively. The variable inter-event time is determined by “ $\lambda * ((\log(1/U))^{(1/\beta)})$ ” through a generated random number “ U ”. The purpose of the randomly generations is to simulate the spill occurrences by time, mass, and NAICS-based location. The MATLAB codes for generating the random variables are summarized in Fig. 4.5.

Generally, the numbers of simulation runs have a direct effect on the accuracy of the simulation

results. Increasing the numbers of runs will reduce the standard error (E_μ) of the mean of a distribution and no effort is made to harness the distribution (Anonym, unknown date). The accuracy only improves as the square root of the ratio of the number of additional runs, which means 100,000 runs instead of 1,000 are needed to achieve an improvement of ten. Through specifying a maximum acceptable percentage error E_μ for the mean, the minimum numbers of simulation runs, n , can be determined by Eq. (3) (Anonym, unknown date).

$$n \geq \left(\frac{\sigma \times z}{E_\mu} \right)^2 \quad (4.1)$$

Where: σ is the true output standard deviation and z is confidence coefficients for different confidence interval (e.g., for 95 and 99% of confidence of normal distribution, and z is 1.96 and 2.58). Since σ is not known, various numbers of n can be performed to find appropriate numbers of simulation runs.

The bigger numbers of simulation runs with longer simulation time period (TP) leads to the longer time simulations. Therefore, it is important to determine the appropriate TP and simulation runs for simulating probabilistic spill occurrences. Ten, twenty, and fifty-year TPs with 10^5 runs were first used in the MMCS model to select the simulation TP. It was found that the benzene spill occurrences over 20 and 50 years were approximately 2 and 5 times respectively, of those occurring over 10 years, which implies that the system of probabilistic spill occurrences could be considered as a steady-state system. Therefore, a 10-year simulation TP is selected for the MMCS model of benzene spill occurrences in the St Clair River AOC, which is also corresponding to the 10-year period of the re-evaluation of Environment Canada's Priority List.

Subsequently, 10^4 , 10^5 , and 10^6 runs with a 10-year TP were input into the MMCS model to select the appropriate simulation runs. It was found that the numbers of benzene spill occurrences with 10^5 , and 10^6 runs were almost the same, while those with the 10^4 runs were slightly different from other two results, which implies that 10^5 or more runs may be big enough for the simulation. Therefore, 10^5 runs were selected for the simulation of benzene spill occurrences in the River AOC. The MCS running ended when occurrence time was outside of 10 years (3650 days) and this loop repeated 10^5 times. The results of the selection of simulation TP and runs are summarized in Table 4.2.

```
% randomly picking up a probability of NAICSi
pick_NAICS = rand;

% randomly picking up an industry from NAICSi by uniform distribution
IND = IND_NAICS_i(randint(1,1,[1,length(IND_NAICS_i)]);

% generating a random number of interevent times ti by Weibull distribution
U = rand(1);
ti = alpha*((log(1/U))^(1/beta));
t = t + ti;      % calculating spill occurrence time

% generating a random number of spilled mass by lognormal distribution
m = lognrnd(mu,sigma);
```

Fig. 4.5: MATLAB codes for generating random variables.

Table 4.2: Summary of simulated benzene spill occurrences in the St Clair River AOC with various simulation time periods and runs.

Simulated Occurrences		NAICS Code			
		325210	325110	324110	Unknown
Simulation Time Period with 10 ⁵ Runs (yrs)	10	5.1	2.2	1.2	2.3
	20	10.1	4.4	2.2	4.5
	50	25.1	11.1	5.2	11.1
Number of Simulation Runs with 10-yr Time Period	10 ⁴	5.0	2.3	1.3	2.3
	10 ⁵	5.1	2.3	1.2	2.2
	10 ⁶	5.1	2.3	1.2	2.2

4.2.3.2. Simulation Results and Discussion

The simulated benzene spill time series including expected spill occurrences, occurrence time, and spilled mass in the St Clair River AOC for the next 10 years are summarized in Table 4.3. Fig. 4.3 (b) describes the frequencies of simulated NAICS codes of benzene spills, whose proportion are 33.3, 31.0, 20.4, 15.3% for the NAICS 325210, Unknown, 324110, and 325110, while Fig. 4.6 (a), (b), and (c) depict the histograms of simulated spill occurrences, occurrence time, and spilled mass respectively of all NAICS groups over 10 years with 10^5 runs. Compared with the observed histogram of NAICS groups, as shown in Fig. 4.3 (a), the frequencies of simulated NAICS groups are slightly different from those of their original values. It can be seen that the NAICS 325210 would produce the highest benzene spill occurrences followed by the NAICS 325110 and the NAICS 324110, which is different from the original arrangement of the NAICS 325210, the NAICS 324110, and the NAICS 325110. This result may assist various levels of government (e.g. local and regional) in implementing management measures and allocating resources (e.g. finance, human resources, equipment and materials) for spill prevention, control and emergency response. As indicated in Section 3.3.3.2, there is a big difference between the maximum and the minimum benzene spilled masses in the NAICS 324110 group, leading to a very large value of standard deviation as shown in Table 4.3. After examining the distribution of simulated spill occurrences using the maximum likelihood method, the four simulated NAICS groups were found to be properly described by normal distributions. Their probability distribution functions (PDF) with their parameters (μ and σ) are illustrated in Fig. 4.6 (d). Therefore, the NAICS-based probabilities of having specific number of inland occurrences could be determined through their normal PDFs. Furthermore, it is observed that more than 90% of simulated masses of all NAICS groups have relatively small values, which

may be attributed to the factor that most of historical spilled masses are relatively small (see the medians and 90th percentiles in Table 3.3).

Table 4.3: Simulation results of benzene spills in the St. Clair River AOC for a 10-year time period (10^5 of simulation runs).

NAICS Group		325210	325110	324110	Unknown
Simulated Occurrence Time (day)	Mean	1817	1834	1573	1758
	St. Dev.	1058	1051	1117	1078
Simulated Spilled Mass (kg)	Mean	126	26	687	15
	St. Dev.	498	69	23705	23
Simulated Occurrences		5.1	2.3	1.2	2.2

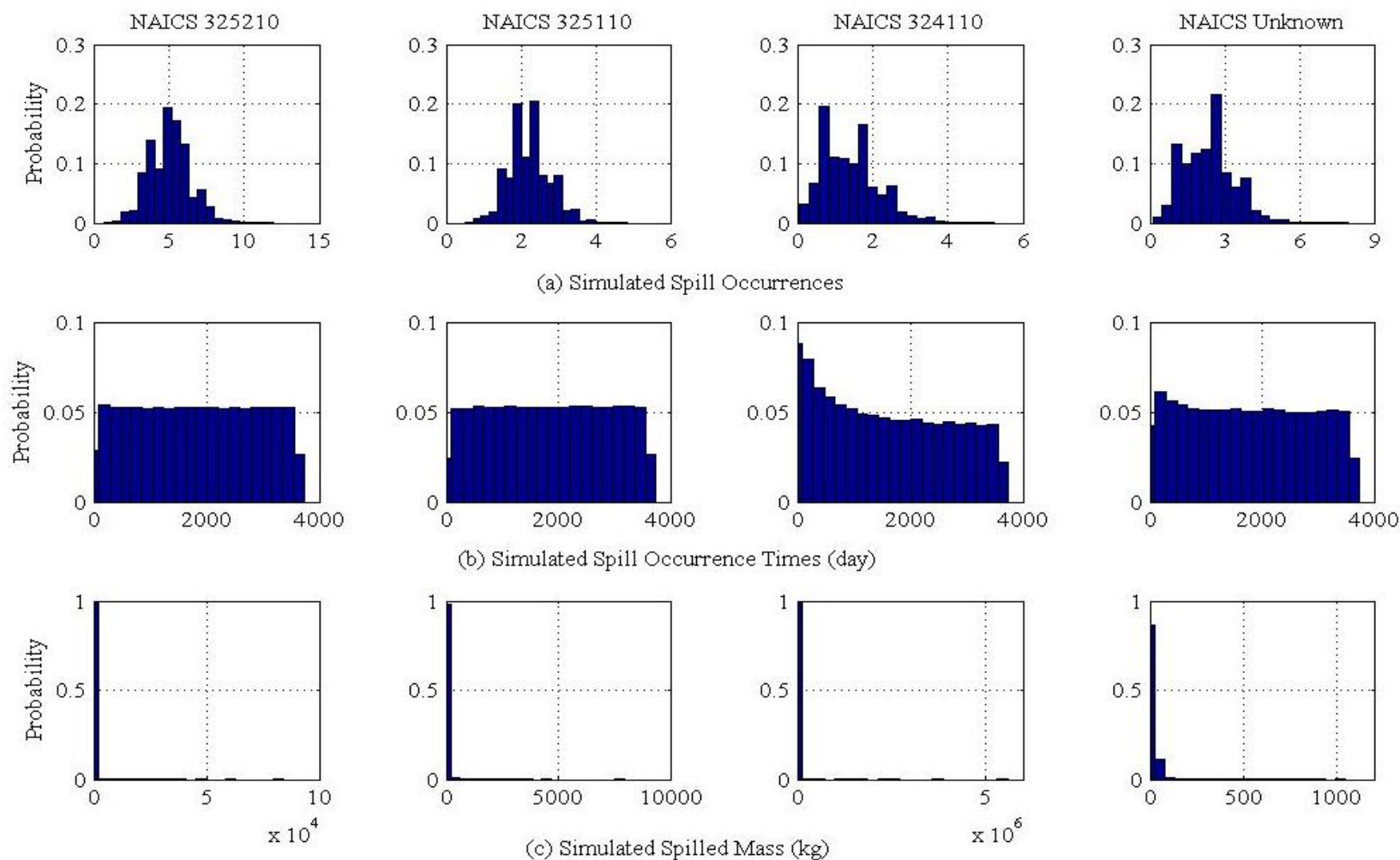


Fig. 4.6: Histograms of simulated benzene spills in the St Clair River AOC for NAICS groups for a 10-year time period (10^5 of simulation runs): (a) Simulated spill occurrences; (b) Simulated spill occurrence time; (c) Simulated spilled mass.

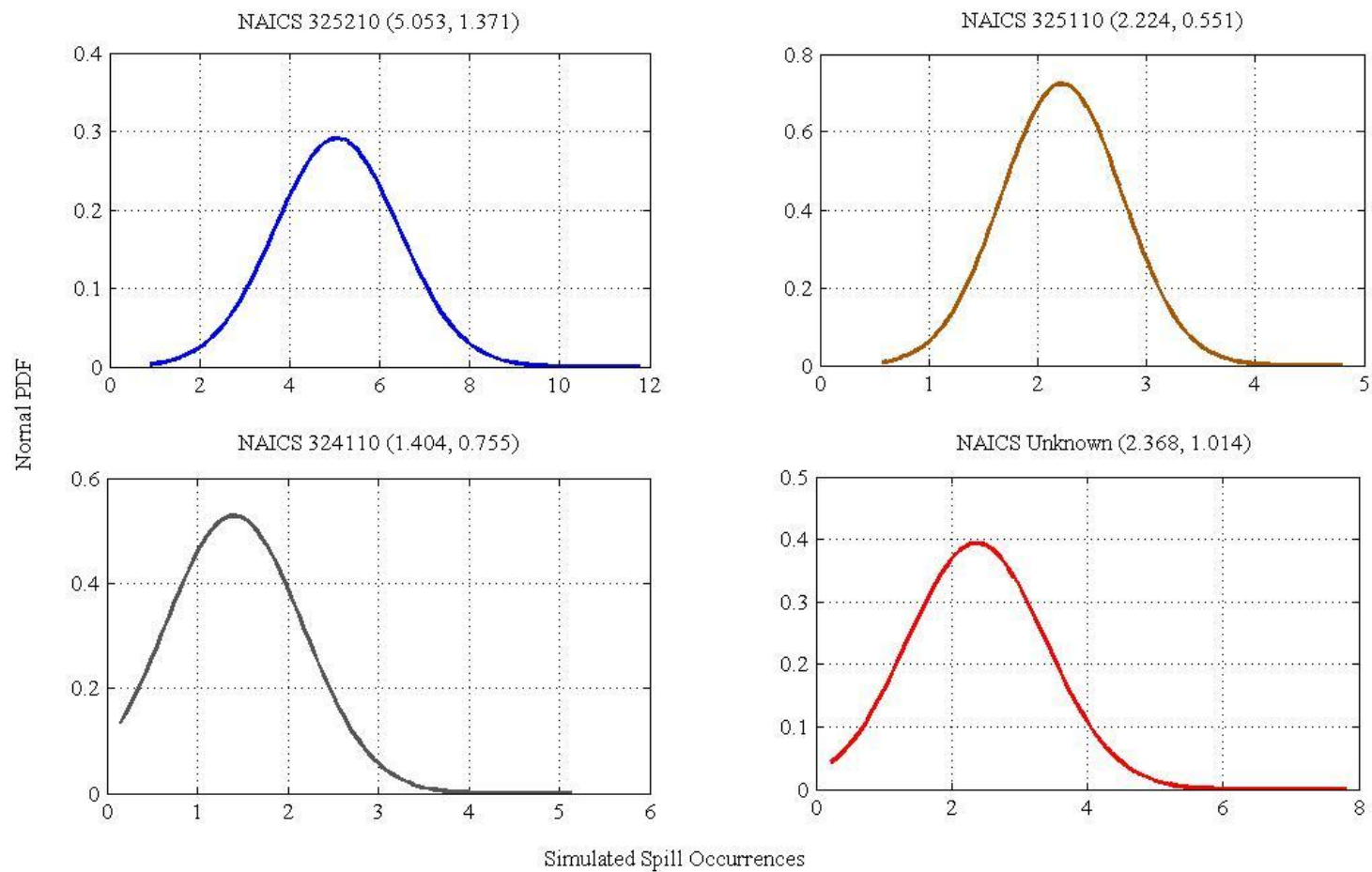


Fig. 4.6 (d): Fitted NAICS-based normal PDF of simulated spill occurrences for a 10-year time period and associated distribution parameter (μ , σ).

4.2.3.3. Uncertainty Analysis

In terms of the occurrences of inland chemical spills, they exhibit both aleatory uncertainties in time and space due to their feature of randomness and epistemic uncertainties due to the inadequate representation of historical spill data. They can arise from the determination of PDs and their involved variable parameters (i.e. NAICS-group, inter-event time, and spilled mass) and spill database limitations (e.g., the estimate errors of spill quantity, inconsistency and non-homogeneity of spill data, the errors of spill data handling and transcription, and inadequate representation of data sample due to time and space limitations). In this research, only the uncertainties of the PD's parameters of all variables and inadequate representation of spill data through bootstrap resamples were investigated.

As discussed in Sections 2.5 and 2.6, a bootstrap resample was repeated one thousand times to analyze the uncertainty of the distributional parameters. Each time a MCS was performed following the MMCS model (as shown in Fig. 4.1), a subset of benzene spill inter-event time and spilled mass were first generated by using nonparametric unbalanced bootstrapping technique for each NAICS group. The PDs of these bootstrapped subsets had the same distributions of Weibull and lognormal for inter-event time and spilled mass respectively. The PD parameters were then estimated by using the maximum likelihood method and NAICS based simulated spill occurrences, mean spill occurrence time and mean spilled mass over 10 years were obtained. The histograms of 1000 bootstrapped replications of simulation results, including simulated spill occurrences, mean spill occurrence time, and mean spilled mass over 10 years, are depicted in Fig. 4.7 (a), (b) and (c). After examining the histograms of various bootstrapped sample statistics, it was found that the PD of the simulated spill occurrences and the means of spill occurrence

time and spilled mass of each NAICS group could be described by lognormal distributions by using the maximum likelihood method. The sample mean, standard deviation, skewness coefficient, and 95% confidence interval of the simulated spill occurrences and the means of occurrence time and spilled mass of each replication are shown in Tables 4.4, 4.5, and 4.6 respectively.

Table 4.4: Bootstrapped resampling statistics of simulated spill occurrences in the St. Clair River AOC over 10 yrs (10^5 of simulation runs).

NAICS Group	Mean	St. Dev.	Skewness Coeff.	95% Confidence Interval	
				Lower Bound	Up Bound
325210	6.5	2.9	1.5	6.3	6.7
325110	2.7	1.4	2.4	2.6	2.8
324110	2.4	4.1	6.1	2.1	2.6
Unknown	2.6	2.9	3.3	2.5	2.7

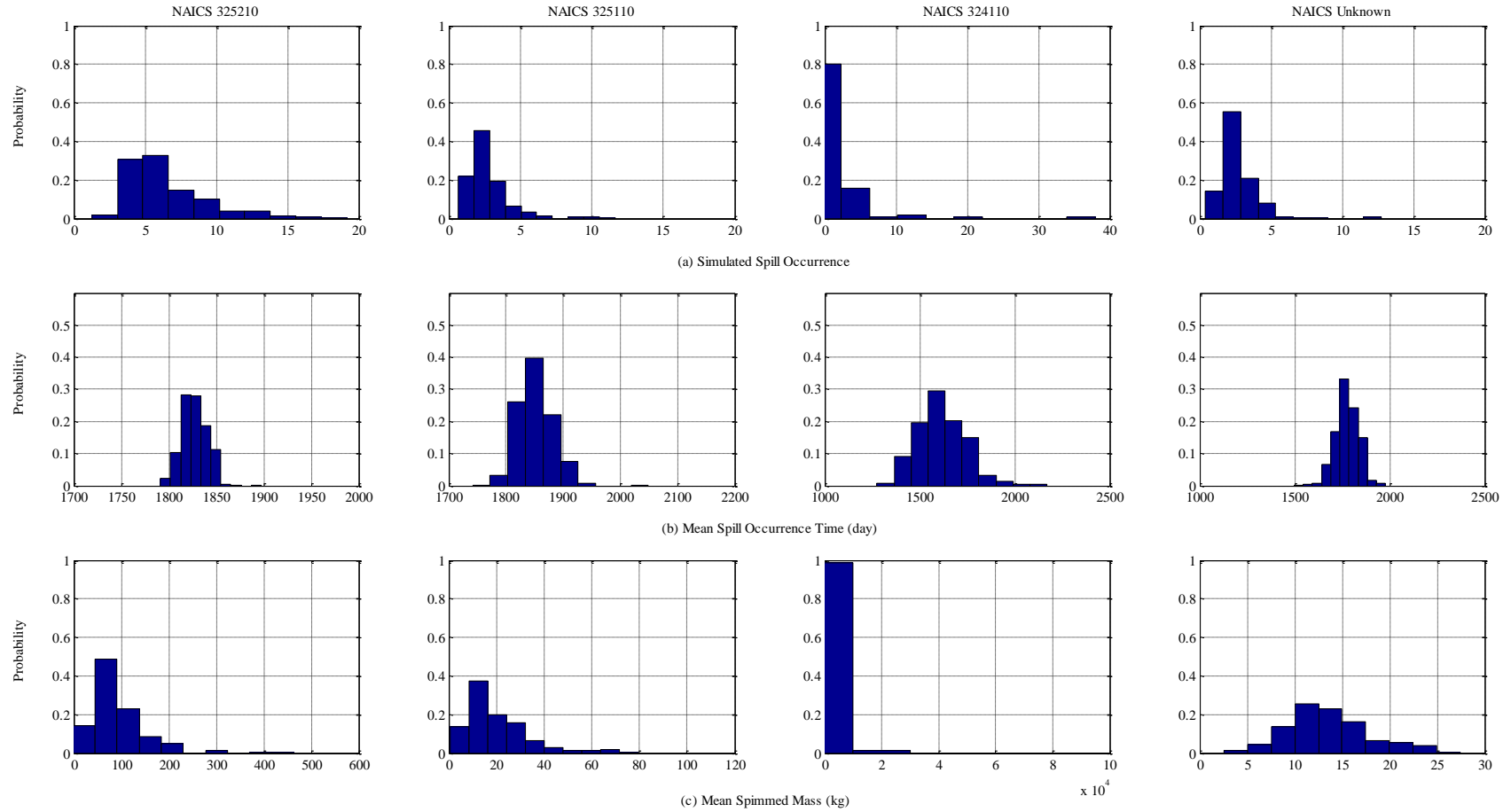


Fig. 4.7: Histograms of 1000 bootstrapped replications of simulated spill occurrences, means of mean spill occurrence time and mean spilled mass for a 10-year time period in the St Clair River AOC (10^5 of simulation runs): (a) Simulated spill occurrences, (b) Mean spill occurrence time, and (c) Mean spilled mass.

Table 4.5: Bootstrapped resampling statistics of mean of mean occurrence time over 10 yrs (10^5 of simulation runs).

NAICS Code	Sample Statistics	Mean (day)	St. Dev. (day)	Skewness Coeff.	95% Confidence Interval	
					Lower Bound	Upper Bound
325210	Mean	1,827.378	12.971	0.342	1,826.575	1,828.182
	St. Dev.	1,052.164	6.876	-0.466	1,051.738	1,052.590
325110	Mean	1,850.916	31.108	0.474	1,848.988	1,852.844
	St. Dev.	1,038.814	17.196	-0.516	1,037.748	1,039.880
324110	Mean	1,615.101	127.710	0.535	1,607.186	1,623.017
	St. Dev.	1,105.992	28.021	-2.942	1,104.255	1,107.729
Unknown	Mean	1,775.327	12.971	-0.140	1,771.583	1,779.071
	St. Dev.	1,070.535	21.440	-0.655	1,069.206	1,071.864

Table 4.6: Bootstrapped resampling statistics of mean of mean spilled mass over 10 yrs (10^5 of simulation runs).

NAICS Code	Sample Statistics	Mean (kg)	St. Dev. (kg)	Skewness Coeff.	95% Confidence Interval	
					Lower Bound	Upper Bound
325210	Mean	91.045	52.350	1.859	87.800	94.289
	St. Dev.	273.543	311.438	3.470	254.241	292.846
325110	Mean	19.632	12.861	1.652	18.835	20.429
	St. Dev.	40.452	59.157	3.798	36.785	44.118
324110	Mean	871.471	6198.629	24.483	487.284	1255.659
	St. Dev.	1.355E+05	2.463E+06	30.698	-1.711E+04	2.882E+05
Unknown	Mean	13.522	52.350	0.588	13.250	13.794
	St. Dev.	18.058	9.400	1.507	17.476	18.641

As indicated in Tables 4.4, 4.5, and 4.6, the bootstrapped resampling distributions for simulated spill occurrences and the means of spill occurrence time and spilled mass of all NAICS groups are skewed to the right (with positive values of skewness coefficient), except for that of mean occurrence time of unknown NAICS which is slightly skewed to left (with skewness coefficient of -0.140), indicating that these data sets are not normal (actually they are lognormal, as discussed above). As shown in Fig. 4.7 (c), about 99% of the NAICS 324110 spilled mass has relatively very small values and small portion has relative large values, leading to a very large standard deviation ($1.355\text{E}+05$). This may be attributed to the existence of a big difference between the maximum and minimum of original benzene spilled masses. The expected values of simulated spill occurrences, occurrence time, and masses based on the original data can provide clues to industries that involved in spills on how frequency potential spills will occur, whether they need to be treated as severe events based on the simulated masses, and when measures (e.g. technologies on site, equipment, and finance, and human resources) need to be ready to deal with them. Moreover, the simulation results also provide support for the next stage of the quantitative risk-based analysis of drinking water quality impairments in the WTP intakes along the St Clair River, which will discuss in Chapter 5.

4.2.4. Simulation of Probabilistic Occurrences of Benzene Spills in the Mimico Creek

4.2.4.1. Model Description

As discussed in Chapter 3, although there were thousands of spills occurred in Southern Ontario for the past two decades, 90% of chemical types happened less than 10 times. This brings

difficulties for investigating the probability distributions of model variables (i.e., spill occurrences, inter-event time, spilled mass) and probabilistic spill occurrences to assist decision making. Therefore, this hypothetical case study is presented to investigate the possibility of the transferrable characteristics of a historical database from one area to another area. The Mimico Creek watershed in the Greater Toronto Area (GTA) was selected to investigate the transferability of the historical benzene spill characteristics in the St. Clair River AOC. The MMCS model simulation for benzene spills in the Mimico Creek watershed applies the same simulation runs (10^5) and time period (10 years) as those in the case of the River AOC. Since NAICS codes are based on “supply-side or production-oriented principles” and are designed “to provide common definitions of industrial structure and a common statistical framework to facilitate the analysis” of the economy (Statistics Canada, 2007), it is hypothesized that industries in the Mimico Creek watershed that have the same NAICS codes as those in the St. Clair River AOC would have same benzene spill potential. A search of Industry Canada and Profile Canada reveals that eight industries have the same NAICS codes, 325210, 325110, and 324110 in the Mimico Creek watershed, and are considered as potential benzene spill sources. Fig.4.8 illustrates the potential sources of benzene spill sources in the Mimico Creek water according to online information in Industry Canada and Profile Canada websites. Similar to the case of the St Clair River AOC, potential spill inter-event time, occurrence times, and spilled mass were assumed to be statistically independent of each other. It was assumed that the PDs determined by the simulation results of NAICS groups (discrete distribution), inter-event times (Weibull distribution), and spilled masses (lognormal distribution) of benzene spills in the River AOC could be transferred to the Mimico Creek watershed. Since the case of the St Clair iver AOC provided an adequate simulated spill database, it was unnecessary to conduct uncertainty

analysis for the parameters of the PDs of inter-event times and spilled masses.

However, since the employee numbers of industries in the St Clair River are much more than those in the Mimico Creek watershed, it is assumed that the manufacturing capacities of the industries in the St. Clair River AOC are much larger than those in the Mimico Creek watershed. Therefore, the spilled masses and other properties that may be produced by potential industries in the Mimico Creek watershed might be much lower. Therefore, in order to obtain the parameters of PDs, the potential masses of benzene spills in the watershed will take a proportion of the historical data in the St. Clair River AOC based on the number of employees of the industries. The reason to choose the employee number to scale the potential spilled masses in the watershed is that there is no information on either industrial manufacturing capacity or production. Based on the online information on industrial employee number from Industry Canada and Profile Canada websites, it is assumed that approximately 1/40, 1/12, and 1/20 of the simulated NAICSs 325210, 325110, and 324110 spilled masses in the River AOC are used to estimate the parameters of lognormal distributions.

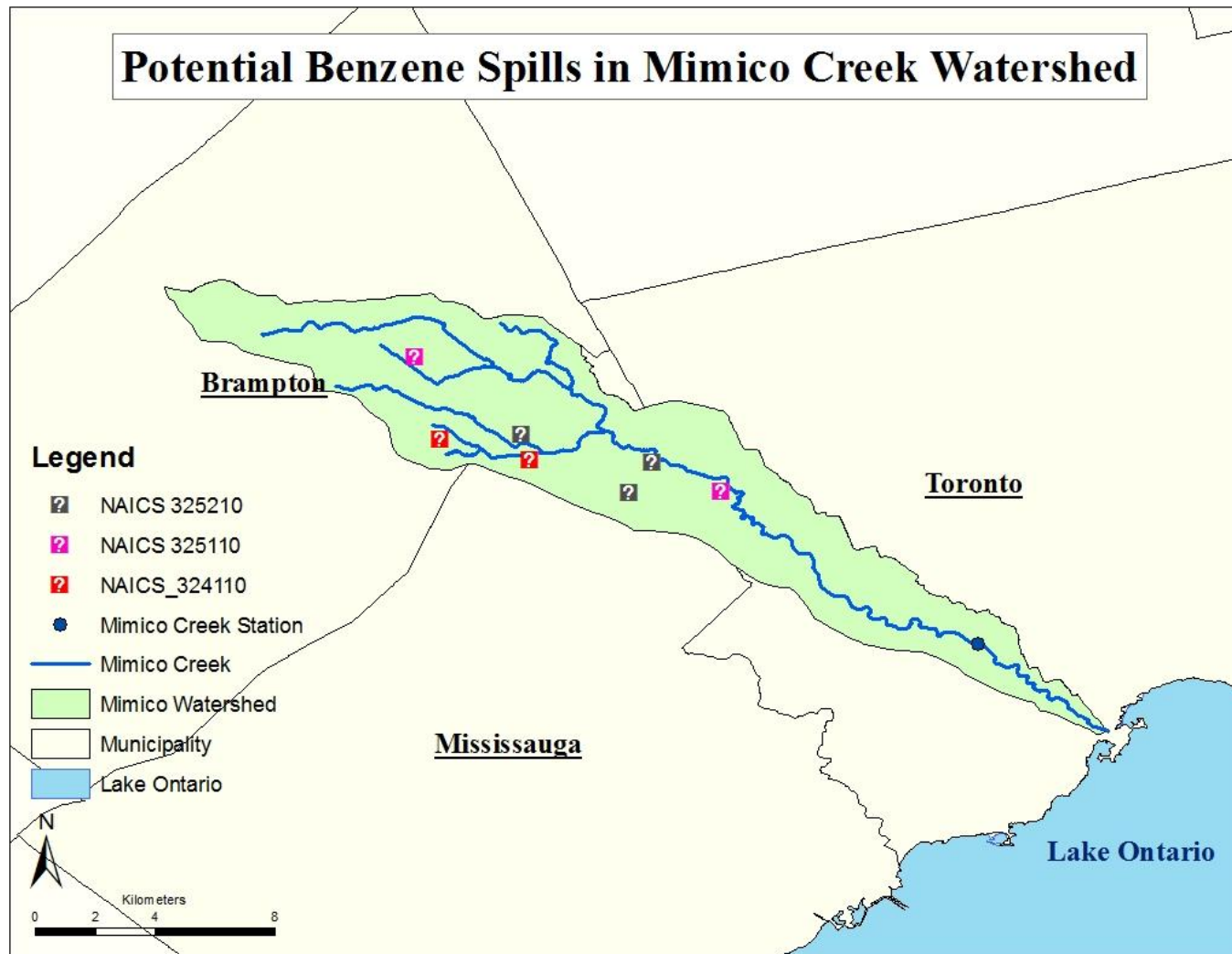


Fig. 4.8: Potential sources of benzene spill in the Mimico Creek watershed according to online information in Industry Canada and Profile Canada websites.

4.2.4.2. Simulation Results and Discussion

The simulated benzene spill time series, including expected spill occurrences, spill occurrence time, and spilled mass, in the Mimico Creek watershed for a 10-year time period are summarized in Table 4.7. As indicated, the NAICS 325210 would be expected to have the highest potential occurrences and violation-causing occurrences followed by the NAICS 325110 and 324110, while the NAICS 324110 would produce the most masses followed by the NAICS 325210 and 325110. The City of Mississauga would potentially experience the highest occurrences and violation-causing occurrences followed by the Cities of Brampton and Toronto, while the City of Brampton would experience the most masses followed by the Cities of Mississauga and Toronto, which may be attributed to the factor that the Cities of Brampton and Mississauga have the industry coded as NAICS 324110 that has high potential spilled masses (see the standard deviation of spilled masses in Table 4.7).

Moreover, if a spill's initial concentration C_o at the outlet to Mimico Creek is estimated by Eq. (4.2), where the volume of benzene spill is negligible compared to the creek's volume.

$$C_o = \frac{M}{Q \times SDT} \quad (4.2)$$

where M is simulated spilled mass, in kg ; Q is the creek's flow rate at the outlet, in m^3/s ; and SDT is spill duration time, in s . It is noticed that the most spill occurrences will cause violation of the maximum acceptable concentration of benzene in drinking water at the outlets to Mimico Creek, indicating that to prevent and control benzene spills at source is highly required regarding water quality protection.

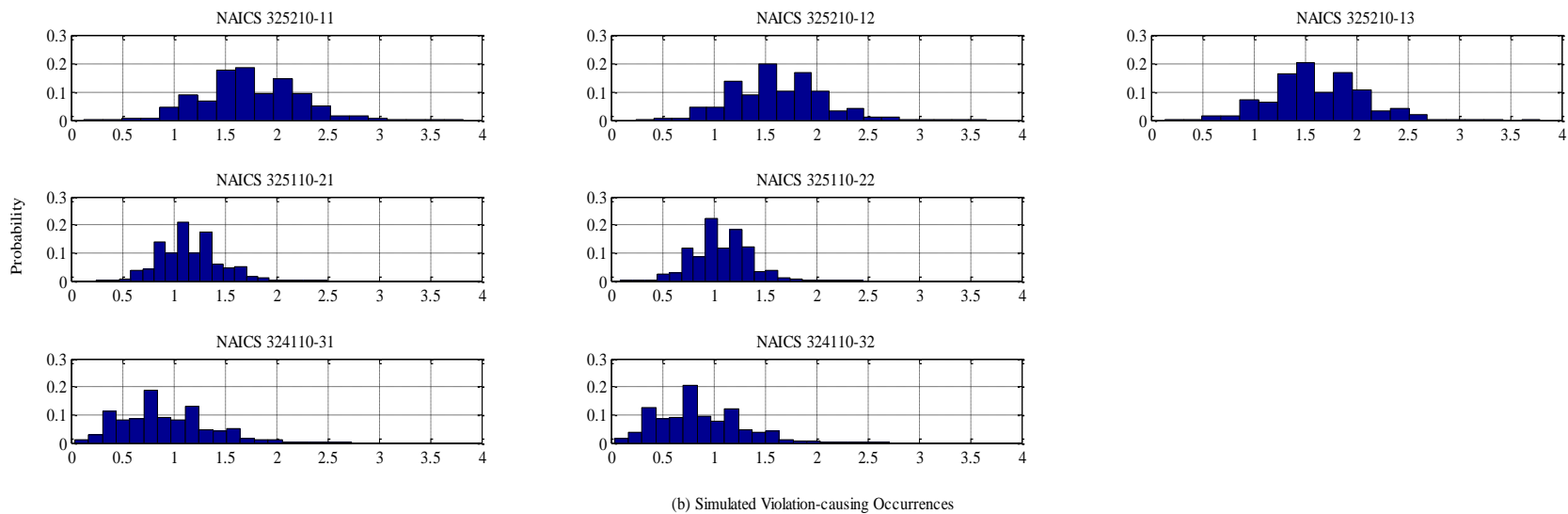
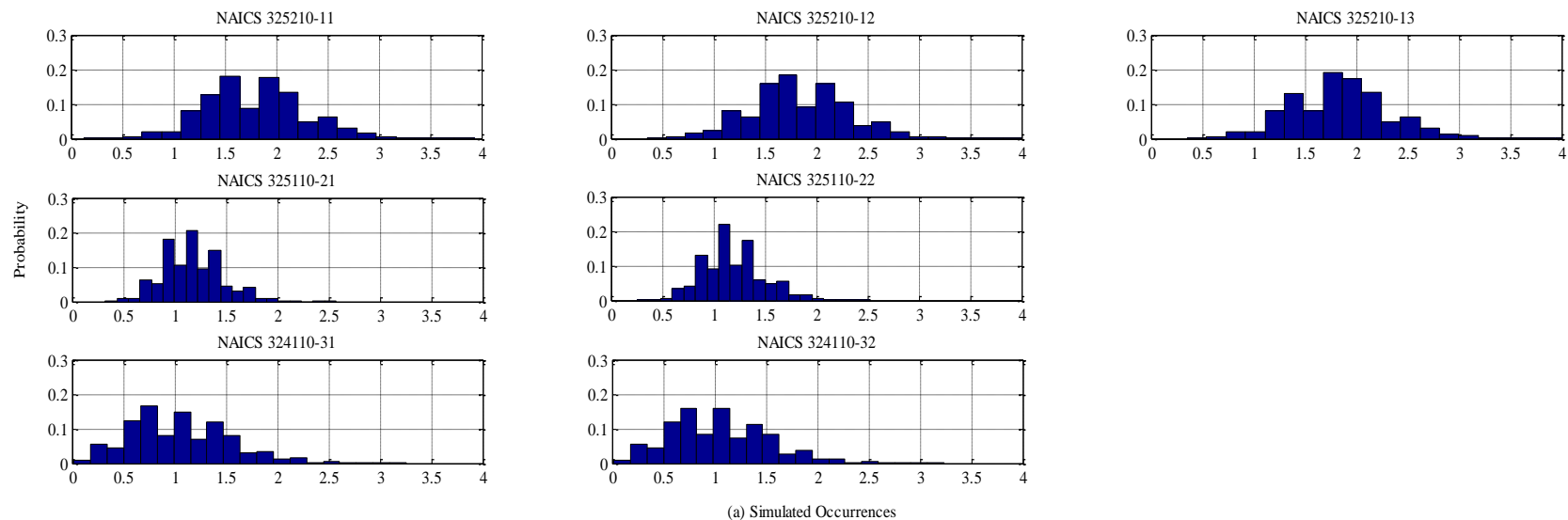
Table 4.7: Simulation results of benzene spill time series in the Mimico Creek watershed for a 10-year time period (10^5 simulation runs).

NAICS Group		325210	325110	324110
Expected Simulated Occurrences		5.5	2.4	2.0
Expected Simulated violation-Causing Occurrence		4.9	2.2	1.7
Simulated Occurrence Time (day)	Mean	1818	1830	1679
	St. Dev.	1056	1051	1099
Simulated Spilled Mass (kg)	Mean	3	2	36
	St. Dev.	12	6	934
Municipality		Mississauga	Brampton	Toronto
Expected Simulated Occurrences		6.5	2.2	1.2
Expected Simulated violation-Causing Occurrence		5.7	2.0	1.1
Simulated Occurrence Time (day)	Mean	1830	1762	1796
	St. Dev.	1051	1075	1065
Simulated Spilled Mass (kg)	Mean	8	18	2
	St. Dev.	332	693	6

The histograms of simulated spill occurrences, violation-causing occurrences, occurrence time and spilled mass for potential individual industries are illustrated in Fig. 4.9. The label of a NAICS code consists of three parts: NAICS code, group number, and industry number. For instance, NAICS 325210-12 represents the second industry in NAICS 325210 classed as group

1. Also, the industries NAICSs 325210-11/12/13 and 324110-32 are in the City of Mississauga, the industries MAICSs 325110-21 and 324110-31 are in the City of Brampton, and the industry NAICS 325110-22 is in the City of Toronto. After examining the distributions of their simulated spill occurrences and violation-causing occurrences by using the maximum likelihood method, it is found that normal distributions could be used to describe them properly, as illustrated in Fig. 4.10. The associated PDF parameters (μ and σ) are shown in Table 4.8. Therefore, the probabilities to have a specific number of inland occurrences caused by industries could be determined through these PDFs.

The histograms of simulated spill occurrences, violation-causing occurrences, occurrence time, and spilled mass by NAICS codes and municipalities are depicted in Figs. 4.11 and 4.12, which indicate that 99% of spilled masses have relatively small values. However, these small values are still significant to the creek's water quality because most of them will violate the maximum acceptable concentration of benzene in drinking water (see Table 4.7). This significance depends on the magnitude of spill, flow rate and geographical characteristics of waterways, water quality model applied, and weather condition. The implications of simulated spills for the water quality of Mimico Creek are discussed in Chapter 5. Similarly, NAICS-based and City-based simulated spill occurrences and violation-causing occurrences are also found to be normally distributed, as shown in Fig 4.13. The associated PDF parameters (μ and σ) are presented in Table 4.8. The simulation results indicate that most simulated spill occurrences by potential industries would cause water quality violation at the outlets to Mimico Creek, which may provide clues to the attitude of industries and/or municipalities with respect to the priority of benzene spill prevention and management.



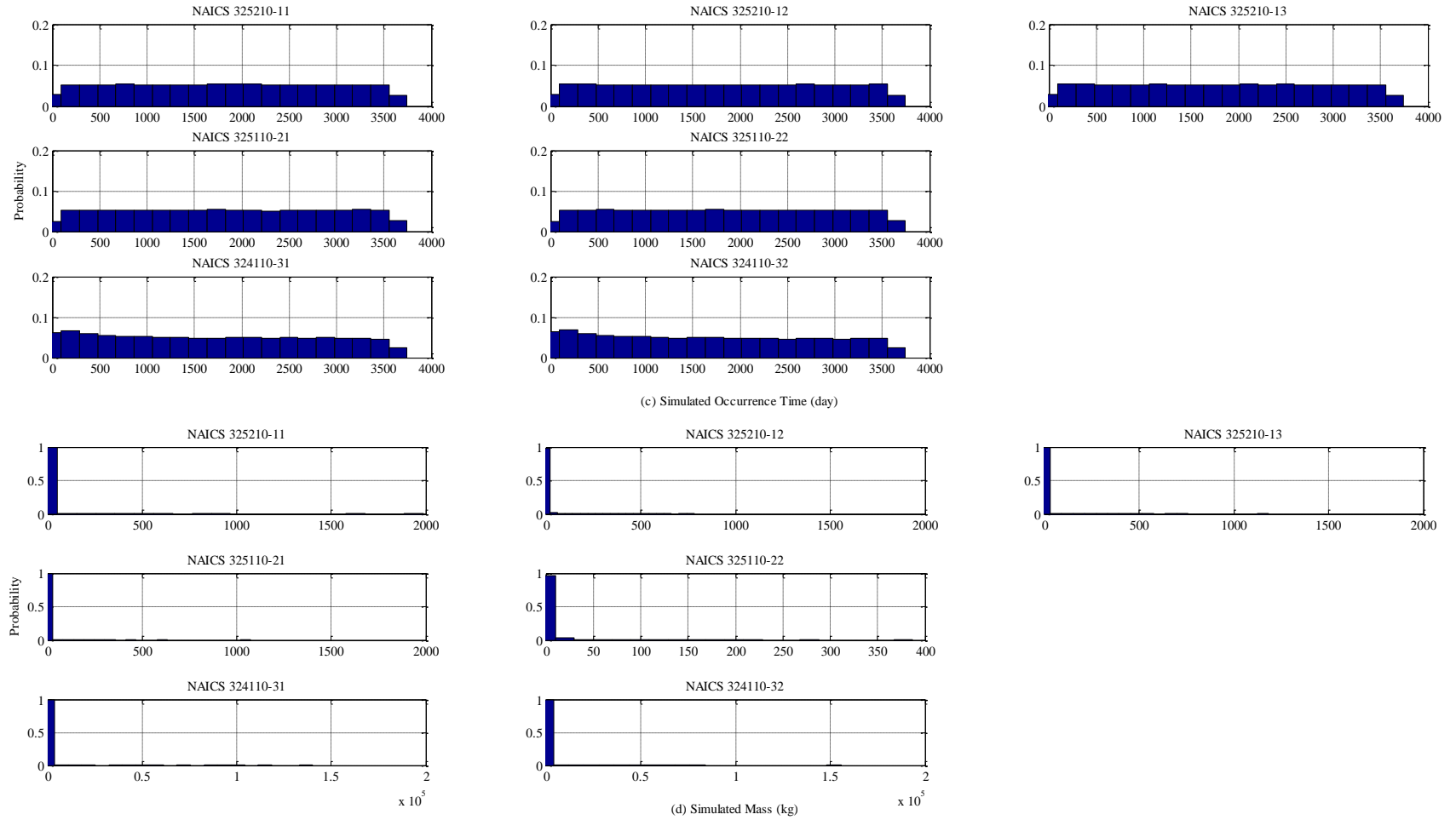


Fig. 4.9: Histogram of potential industries' simulated benzene spills in the Mimico Creek watershed for a 10-year time period (10^5 simulation runs): (a) Simulated occurrences, (b) Simulated violation-causing occurrences, (c) Simulated spill occurrence time, and (d) Simulated spilled mass.

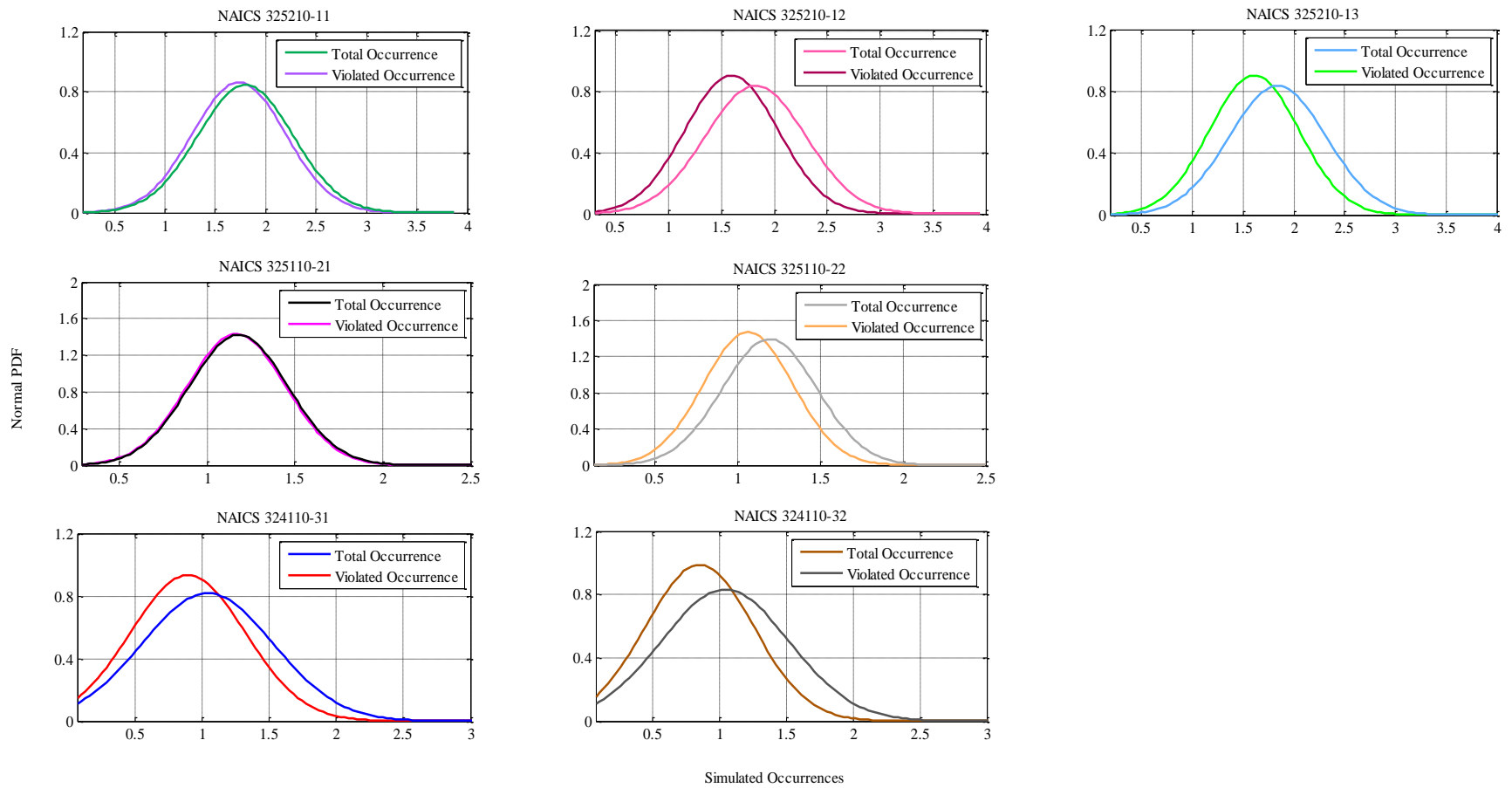
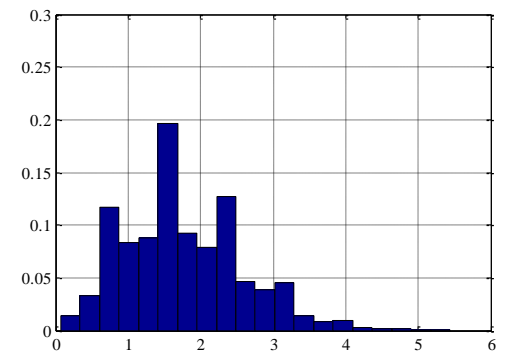
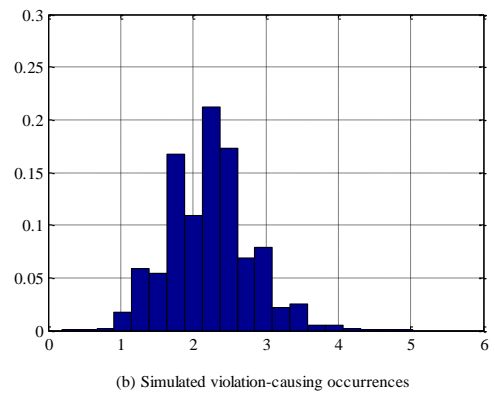
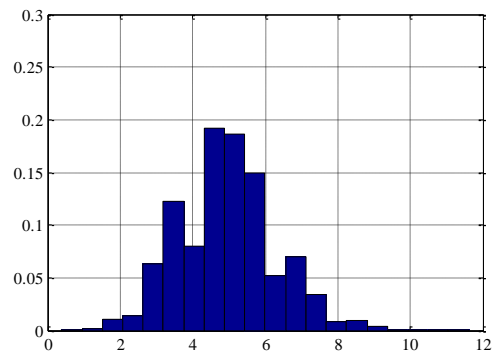
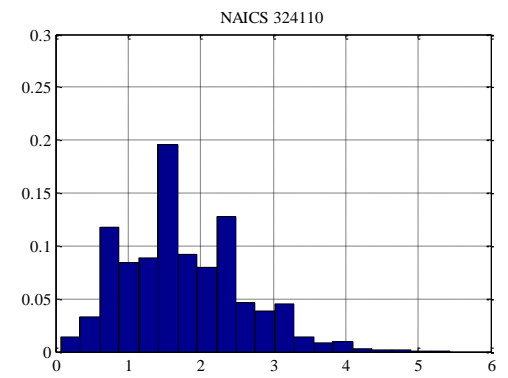
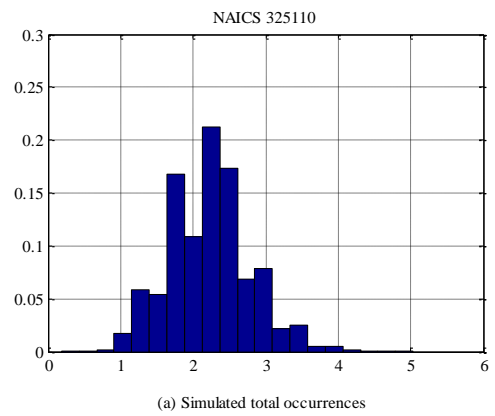
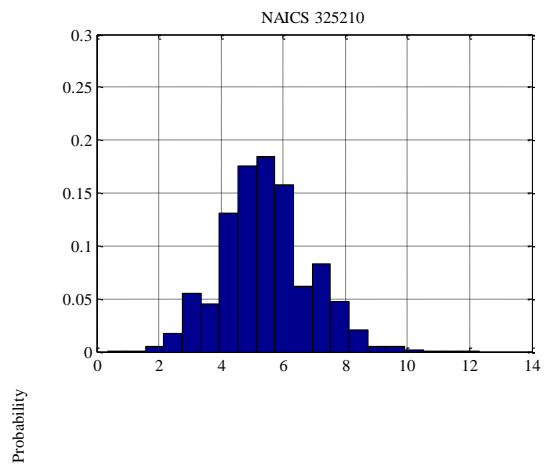


Fig. 4.10: Fitted normal PDFs of simulated spill occurrences of individual industries for a 10-year time period.



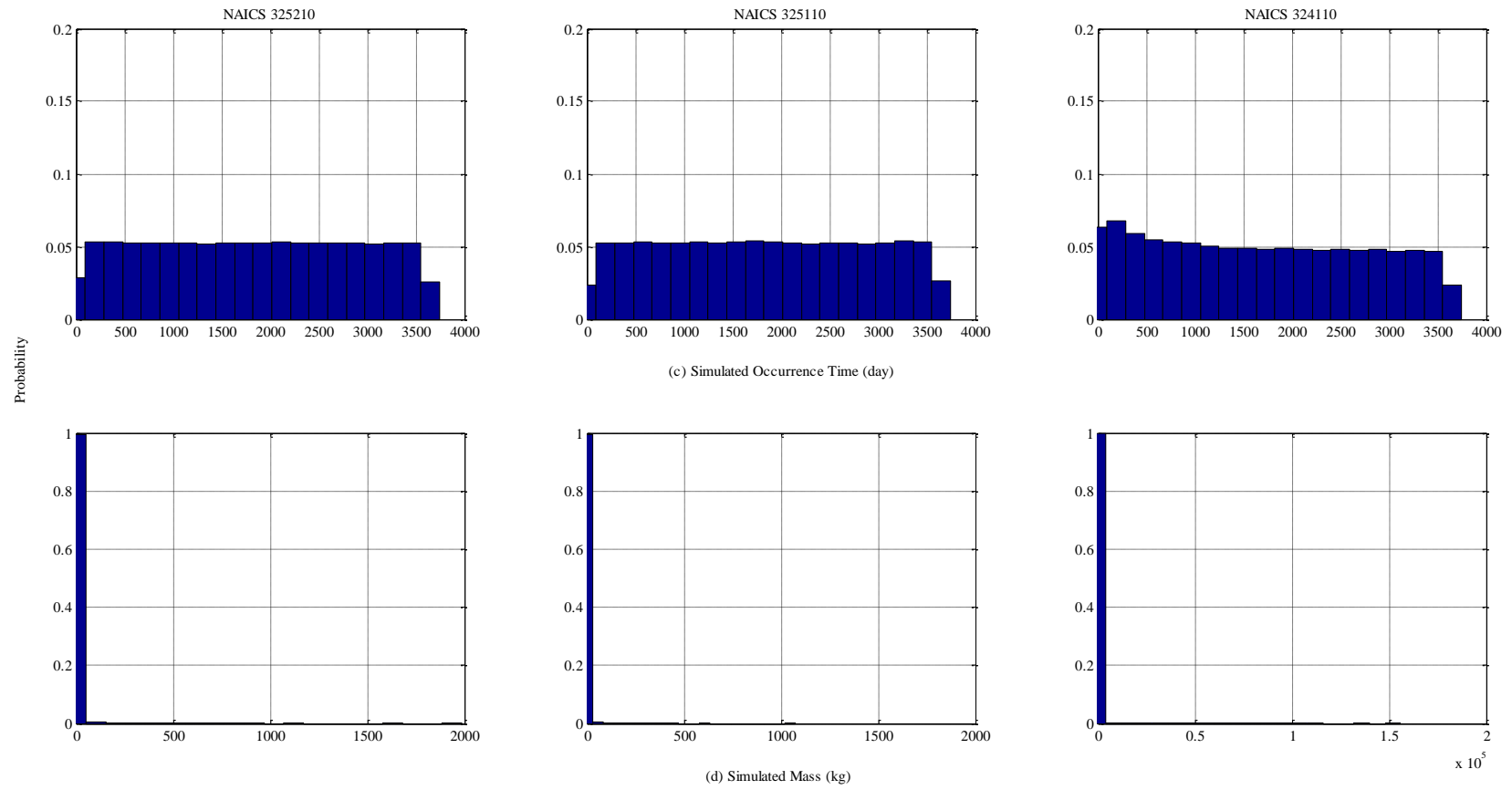
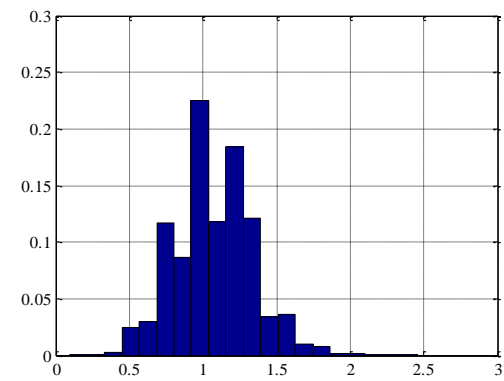
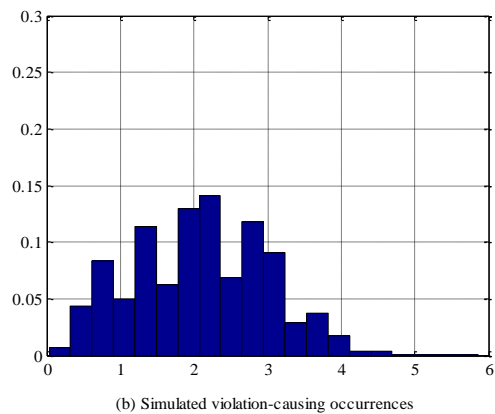
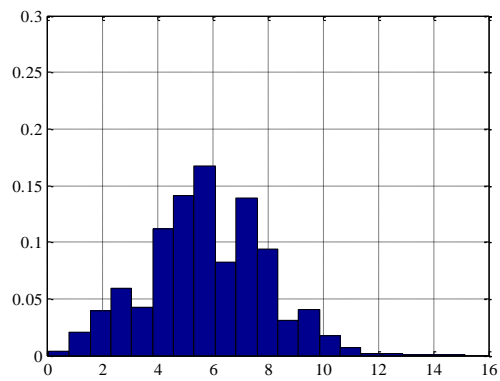
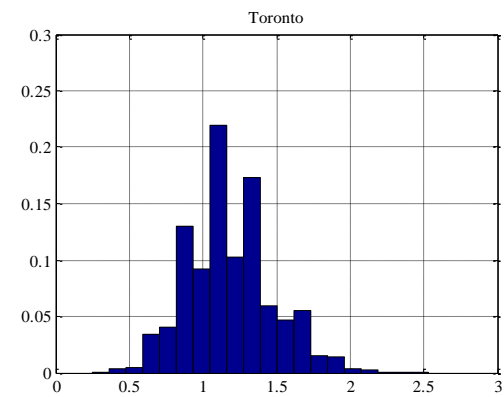
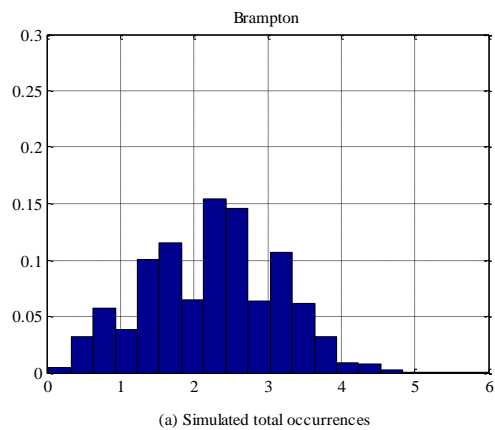
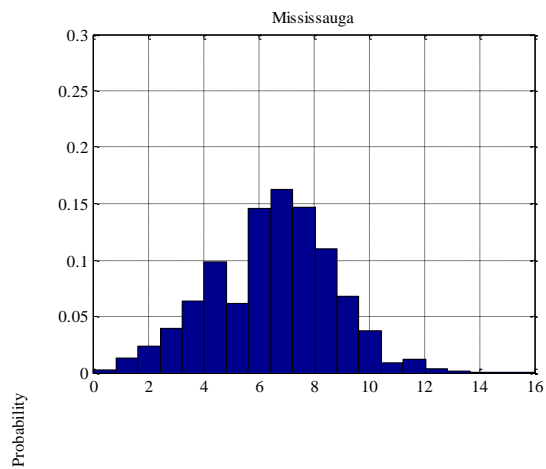


Fig. 4.11: Histogram of simulated benzene spills in the Mimico Creek watershed by municipalities for a 10-year time period (10^5 simulation runs): (a) Simulated spill occurrences, (b) Simulated violation-causing occurrences, (c) Simulated occurrence time, and (d) Simulated spilled mass.



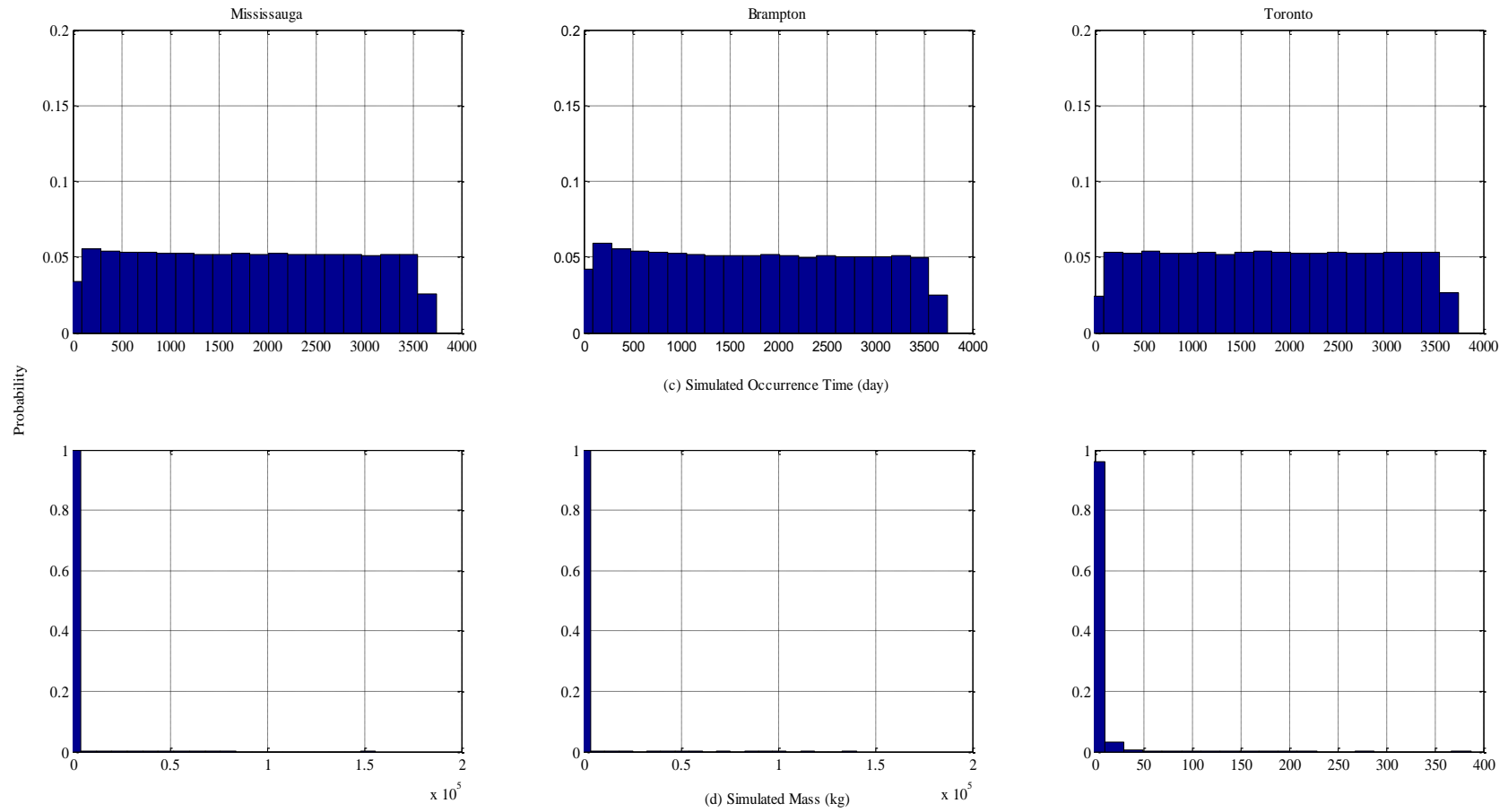


Fig. 4.12: Histogram of simulated benzene spills in the Mimico Creek watershed by NAICS codes for a 10-year time period (10^5 simulation runs): (a) Simulated spill occurrences, (b) Simulated violation-causing occurrences , (c) Simulated spill occurrence time, and (d) Simulated spilled mass.

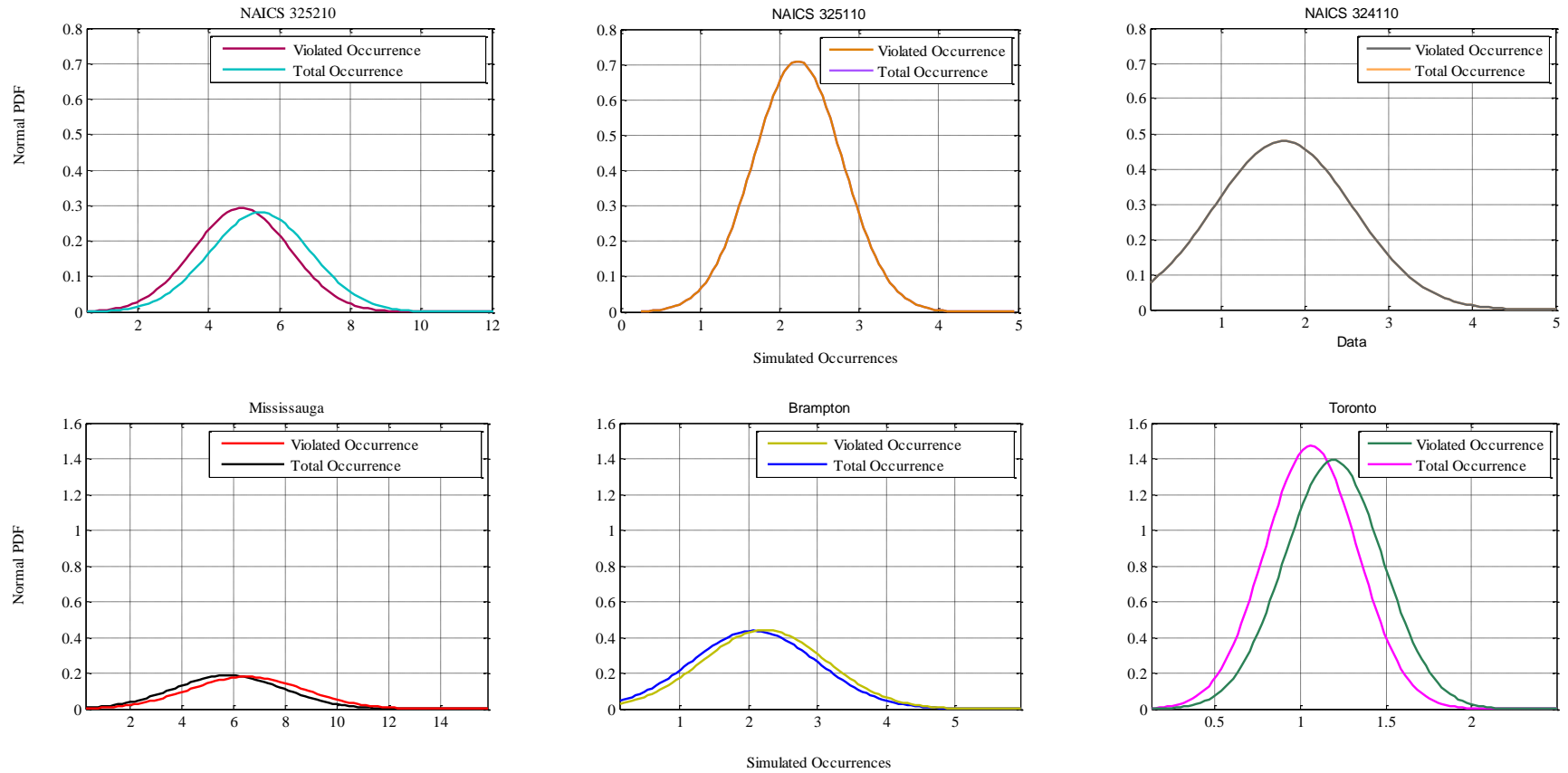


Fig. 4.13: Fitted NAICS-based and City-based normal PDFs of simulated spill occurrences and violation-causing occurrences for a 10-year time period.

Table 4.8: Parameters (μ and σ) of fitted normal PDFs for industries, NAICS codes, and municipalities.

Simulated Occurrences		Total Occurrences		Violation-Causing Occurrences	
Normal PDF Parameter		μ	σ	μ	σ
City	Mississauga	6.517	2.212	5.811	2.124
	Brampton	2.231	0.901	2.076	0.912
	Toronto	1.194	0.286	1.064	0.271
NAICS Code	325210	5.462	1.423	4.938	1.365
	325110	2.229	0.562	2.229	0.562
	324110	1.747	0.833	1.747	0.833
Industry	325210-11	1.799	0.470	1.735	0.461
	325210-12	1.823	0.475	1.593	0.440
	325210-13	1.841	0.478	1.610	0.442
	325110-21	1.178	0.280	1.166	0.279
	325110-22	1.194	0.286	1.064	0.271
	324110-31	1.046	0.488	0.899	0.428
	324110-32	1.039	0.480	0.848	0.404

4.3. Summary of Findings Regarding MMCS Simulations

Based on the above simulation results, the following findings are summarized as:

- The proposed MMCS model is able to simulate probabilistic inland chemical spill occurrences by time, magnitude and NAICS based location.
- The statistical analysis and spatial characteristic of benzene spills in the St Clair River AOC from 1988-2007 showed that only 61% of benzene spills in the St Clair River AOC

had reported quantities, either mass or volume, which were used for investigating probability distributions of the MMCS model variables (i.e. spill inter-event time and spilled mass).

- Three known NAICS based industrial groups (represented by NAICS codes, 325210, 325110, and 324110) involved in the production of benzene, in addition to unknown sources due to the leakage of containers, pipe lines, valves, and fittings, are responsible for surface water pollution and other negative environmental impacts.
- Spill inter-event time and spilled mass, as well as spill occurrence time and spilled mass are found to be statistically independent. Furthermore, the NAICS based spill occurrences, spill inter-event time and spilled mass were properly described by normal, Weibull and lognormal distributions respectively.
- Simulation results of benzene spills in the St Clair River AOC show that over the next 10 years, NAICS 325210 would likely produce the highest spill events (5 occurrences with 1817 days of expected occurrence time and 126 kg of expected spilled mass), followed by NAICS 325110 (2 occurrences with 1834 days of expected occurrence time and 26 kg of expected spilled mass) and NAICS 324110 (1 occurrence with 1573 days of expected occurrence time and 687 kg of expected spilled mass). Comparably, the original arrangement of NAICS based spill occurrences from highest to lowest, excluding unknown sources is NAICS 325210, NAICS 324110, and NAICS 325110.
- The simulation results of one thousand times of bootstrap resampling suggested that benzene spill occurrences and the means of spill occurrence time and spilled masses of all NAICS codes in the St Clair River AOC were lognormal distributed.
- In the forecasted 10 year period, the simulation results indicate two benzene spill

occurrences from unknown sources, indicating that the spill reporting system needs to be improved to avoid unknown information such as industry and location.

- Simulation results of benzene spills in the Mimico Creek watershed suggest that the NAICS 325210 would potentially have the highest occurrences and violation-causing occurrences and the NAICS 324110 would produce the most masses. The City of Mississauga would potentially experience the highest spill occurrences. The NAICS- and City-based simulated spill occurrences and violation-causing occurrences are found to be normally distributed.

CHAPTER 5 QUANTITATIVE RISK ANALYSIS OF WATER QUALITY IMPAIRMENT BY INLAND CHEMICAL SPILLS

This chapter describes an extended MATLAB-based Monte Carlo Simulation (EMMCS) model to quantify the risks of source water quality violation in compliance with associated standards based on the MMCS model developed in Chapter 4. A selected water quality model is integrated into the EMMCS model to compute downstream concentrations of simulated spills along receiving waters. The EMMCS model also integrates nonparametric unbalanced bootstrapping technique to quantify the model's aleatory and epistemic uncertainties. Benzene spills in the St. Clair River AOC and the Mimico Creek watershed (hypothetical case), along with their fates along these waterways, are used as case studies to demonstrate the EMMCS model.

5.1 Methodologies of Quantitative Risk Analysis of Drinking Water Quality Impairments by Inland Chemical Spills

As discussed in the Section 4.2.3.1, the system of probabilistic spill occurrences could be a steady-state system. So the risks due to the spill occurrences were also in the steady-state system. According to the discussion in the Section 2.5, Eq. (2.37) (Ganoulis, 2009) and Eq. (2.38) were used to determine the risk (P_F) of a chemical spill in rivers. Theoretically, estimation of risk requires the determination of all possibilities and therefore it is impossible to find a single universally-acceptable value of risk. With high performance computers, Monte Carlo simulation (MCS) enables the generation of a very large number of random values of a stochastic process according to their probabilistic characteristics and facilitates the estimation of risk. The ratio of

numbers of system failures and total generated numbers of concentrations can be treated as the probability of failure – the risk (P_F). Therefore, Eq. (2.44) reduces to Eq. (5.1). Considering n mutually exclusive events, the probability of at least one failure occurrence can be determined by Eq. (5.2), namely overall failure probability (TP_F). Therefore, Eq. (5.3) is derived from Eq. (5.2) in the MCS.

$$P_{F|MCS} = \frac{N_F}{N} \quad (5.1)$$

$$TP_F = 1 - (1 - P_{F_1})(1 - P_{F_2}) \dots (1 - P_{F_n}) \quad (5.2)$$

$$TP_{F|MCS} = 1 - (1 - \frac{N_{F_1}}{N_1})(1 - \frac{N_{F_2}}{N_2}) \dots (1 - \frac{N_{F_n}}{N_n}) \quad (5.3)$$

where

- N_F is number of times the system fails where $C > C_s$;
- N is total number of C ;
- N_{F_2}, \dots, N_{F_n} is number of times that the system fails for event 1, 2, ... n, respectively, where $C > C_s$; and
- N_1, N_2, \dots, N_n is total number of event 1, 2, ... n, respectively.

The EMMCS, which provides a quantitative risk analysis of drinking water quality violation due to NAICS-based inland chemical spills, is depicted in Fig. 5.1. The model first simulates NAICS-based spill time series and assumes simulated spill masses are directly into rivers or waerway, then computes their concentrations at downstream locations using a water quality model, and finally determines the NAICS-based risk and overall risk of water quality violation in compliance with associated standards. Prior to running the EMMCS model, the correlations

among variables related to a spill (i.e. NAICS-based location, inter-event time, occurrence time, spilled mass, and river flow) are needed to be examined using regression analysis. To estimate the risk of a NAICS-based spill to a river, the statistical variations are required to be included in the EMMCS: the probability distributions (PDs) of NAICS-based locations which may be represented by frequency distribution, inter-event time, spilled mass and river flow, concentration after initial dilution (if needed), and downstream expected concentrations at given locations.

5.2 Case Studies

5.2.1 Risks of Drinking Water Quality Violation due to Benzene Spills along the St. Clair River

According to SLEA database, benzene spills generated by various facilities in the St Clair River AOC have been reported to enter directly or indirectly to the river leading to 6 shutdowns of WTPs during the period of 1990-2004. With respect to unknown or expected risk to public health, 0.005 mg/L of MAC is set out for benzene in drinking water (Ontario MOE, 2002), which is used as a standard concentration (C_s), as presented in Eq. (3.22), in the EMMCS model for the quantitative risk analysis of drinking water quality.

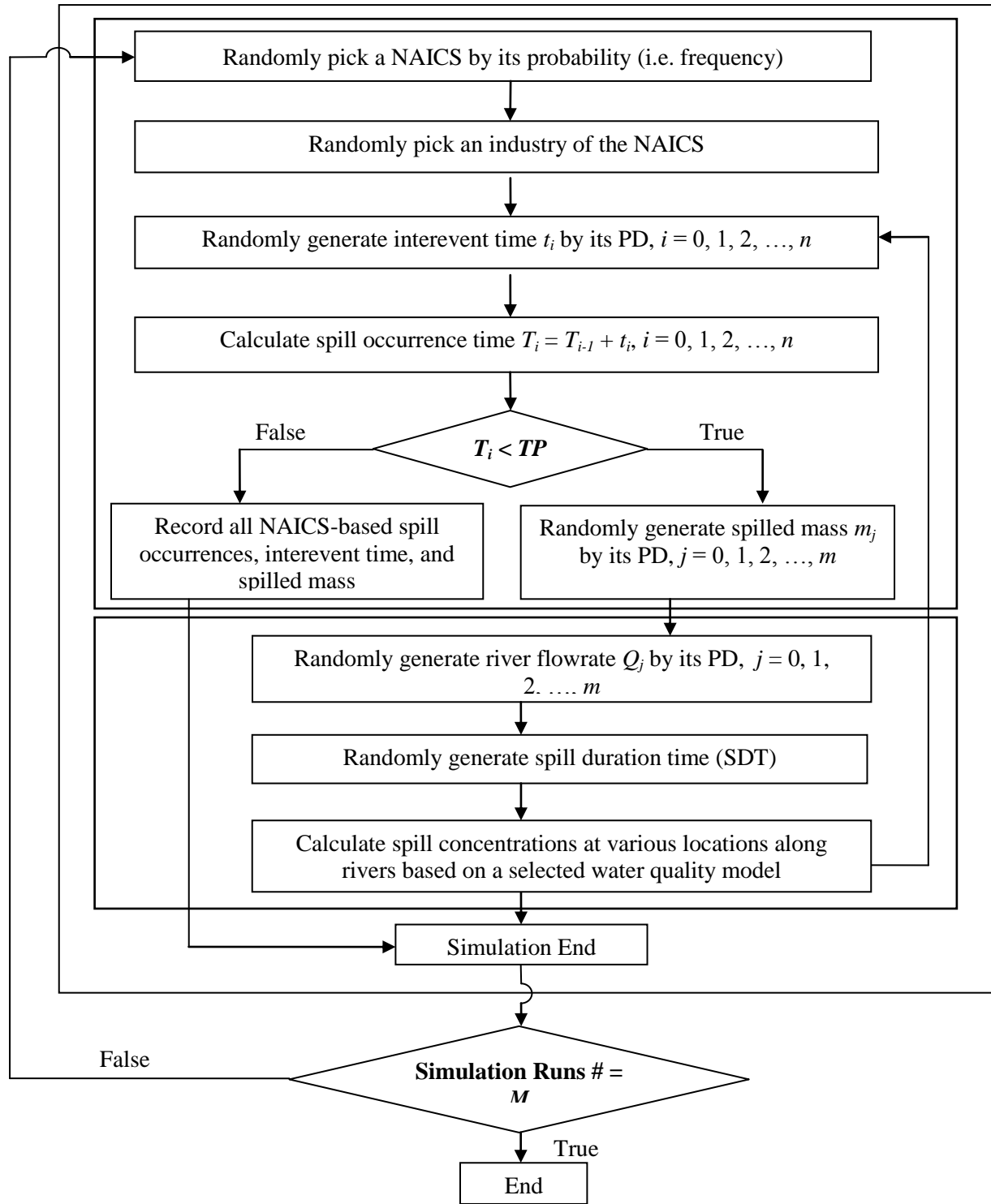


Fig. 5.1: Extended MATLAB-based Monte Carlo simulation (EMMCS) model for quantitative risk analysis of water quality impairments due to inland chemical spills (M and TP represent the numbers of simulation runs and simulation time period).

5.2.1.1 Background of the St. Clair River

The St. Clair River is located in central North America and forms part of the international boundary between Ontario in Canada and Michigan in the U.S. It connects the southern end of Lake Huron to the northern end of Lake St. Clair with 65.2 km of length (U.S. Geological Survey, 2011). The River drops almost 1.5 *m* and its water travels 21 hours from Lake Huron to Lake St. Clair (U.S. Army Corps of Engineers, 2004). According to historical records, the flow is relatively consistent with the annual average discharge of 5,510 m³/s. The periods of abnormally high or low water supplies from Lake Superior, Lake Michigan and Lake Huron usually cause the extreme river flow fluctuation between a maximum of 6,570 m³/s and a minimum of 3,000 m³/s. The river flow is also reduced significantly in winter and early spring for weeks at a time by ice buildup in the lower river. The River drains 576,000 km² (U.S. Army Corps of Engineers, 2004) and is the primary drinking water source for a number of Canadian and U.S. communities (Esman, 2008). The River was designated an Area of Concern (AOC) in 1987 under the Canada–United States Great Lakes Water Quality Agreement because of its primary pollutants such as bacteria, heavy metals, toxic organics, contaminated sediments, fish consumption advisories, impacted biota, and beach closings (Environment Canada, 2010; U.S. EPA, 1995). Actually, there are 450 petrochemical facilities located within a 30 km stretch of the St. Clair River (Ontario MOE, 2005), which become the sources of potential spills bringing potential threats to water quality.

5.2.1.2 Correlations and Probability Distributions of EMMCS Model

Variables

Chapter 3 presents statistical analysis and spatial characteristics of benzene spills in the St Clair

River AOC. Three known NAICS-based industrial groups, NAICS 325210, 325110, and 324110, which involved in the production of benzene spills, in addition to unknown sources had been used in Chapter 4 to demonstrate the MMCS model. Fig. 3.10 depicts the benzene spill outfalls of the 3 known NAICS groups, in addition to 11 WTP intakes (on both the Ontario and Michigan sides) along the St Clair River. In this figure, the intakes on the Ontario side from upstream to downstream are Stag Island, Lambton Generating Station, Fawn Island, Head of Chenal Ecarte, Walpole Island, and Wallaceburg, while that of the intakes on the Michigan side are St. Clair, East China Township, Marine City, Algonac, and Old Club. The unknown source was assumed to be any one of the known sources. According to results from Chapter 4, the spill inter-event time, occurrence time, and spilled mass of each NAICS group in the St Clair River study area were found to be statistically independent of each other. Furthermore, the correlation between benzene spilled masses and the River's daily flow rate was examined by using regression analysis. A very low coefficient of determination (R^2) of 0.032 is obtained. Therefore, statistical independence was assumed between the River's flow and any one of the spill related variables (i.e. NAICS-based location, inter-event time, and spilled mass).

The St. Clair River daily flow rates between 1988 and 2007 were provided by Environment Canada. Using the maximum likelihood method, various probability distributions, including normal, lognormal, Weibull, exponential, and Gamma, were tested for the goodness-of-fit for the PDs of monthly flow rates, and the minimum and maximum monthly based daily flow rates of the River. It was found that the PDs of the monthly flow rates could be properly described by the lognormal distribution. Fig. 5.2 shows the fitted monthly flow rates, and their parameters are summarized in Table 5.1. The PDs of both the minimum and the maximum monthly based daily

flow rates were found to be better fitted with the Weibull distributions.

Table 5.1: Estimated parameters of the lognormal distributions of month-based daily flowrates in the St. Clair River by using MATLAB functions.

Month	μ_y	σ_y	Month	μ_y	σ_y
Jan	8.5358	0.0976	Jul	8.6129	0.0850
Feb	8.5247	0.0967	Aug	8.6183	0.0834
Mar	8.5384	0.0958	Sept	8.6063	0.0892
Apr	8.5723	0.0935	Oct	8.5970	0.0894
May	8.5913	0.0921	Nov	8.5879	0.0928
Jun	8.5358	0.0976	Dec	8.5694	0.0988

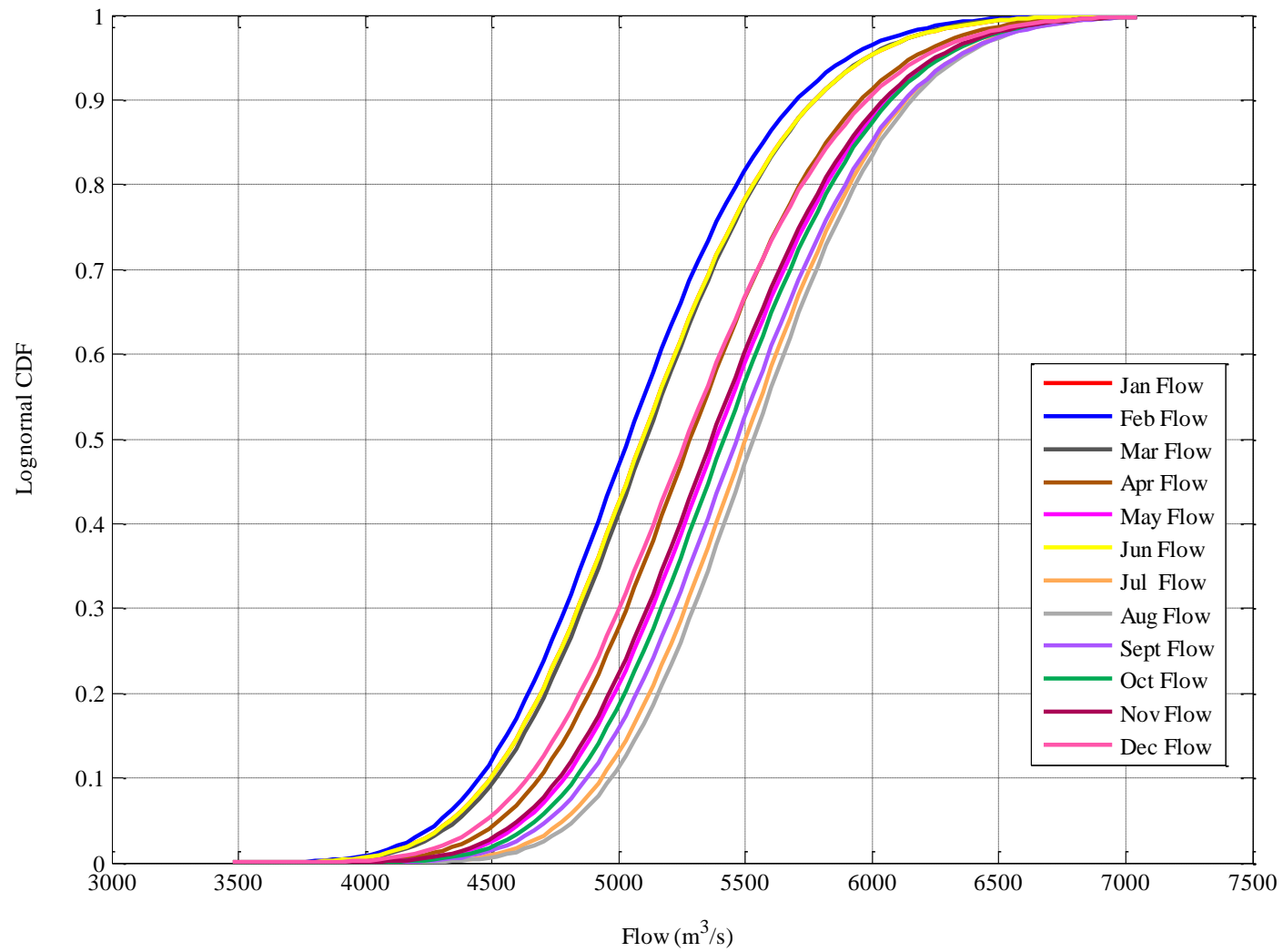


Fig. 5.2: Fitted lognormal cumulative month-based daily flowrates in the St. Clair River.

5.2.1.3 Water Quality Models

The calibrated SpillMan model (Nettleton and Hamdy, 1988) was employed to estimate the peak concentrations of simulated benzene spills, their arriving time, and the arriving/departure time of spill plumes at the 11 WTP intakes along the St Clair River, including both 6 intakes in Ontario (Stage Island – 14 km from riverhead, Lambton Generating Station – 25 km, Fawn Island – 36 km, Head of Chenal Ecarte – 43 km, Walpole Island – 46 km, and Wallaceburg – 55 km) and 5 intakes in Michigan (St. Clair – 22 km from riverhead, East China Township – 30 km, Marine City – 34 km, Algonac – 46 km, and Old Club – 63 km). The SpillMan model assumed that the St Clair River has complete vertical mixing and it provided relatively rapid and easy-to-use assessment techniques to predict the peak concentrations of a spilled contaminant depending on a spill duration time (SDT) at the WTP intakes. Due to the lack of information on the flow rate of spills entering the River, it is assumed that all spilled masses are received by the River without any inland losses, which provides a maximum result.

Based on Eqs. (2.14) to (2.19), Nettleton and Hamdy (1988) used the actual results of several past projects carried out by the Ontario Ministry of the Environment and tabulate them for two conditions – 6,800 and 5,300 m³/s river flow rates in order to use the SpillMan model rapidly and easily. These tables include the following tables and are presented in Appendices A.1.1 to 1.6.

- Mean travel time (TT, in hr);
- Critical spill duration time (TC, in hr), which was used to determine a spill type – short-duration spill or long-duration spill at an outfall;
- Time between arrival and peak or peak and departure (TAPD, in hr);
- General decay factors (DF, in s⁻¹), which was used in correcting the predicted

concentrations for decay loss at various TT;

- No-decay peak concentration for a loading rate of 1 kg/s (PC, in ug/L), which was applied to determine predicted peak concentrations at an intake, as shown in Eq. (5.4), and the arrival time of the decay-corrected peak concentration (TPK) and the spill plume's arrival and departure times (TAPL and TDPL, in hr) at an intake are determined by Eq. (5.5) to (5.7);

$$CPC = M \times PC \times NUMDSF \quad (5.4)$$

$$TPK = TT + \frac{T}{2} \quad (5.5)$$

$$TA = TT - TAPD + \frac{T}{2} \quad (5.6)$$

$$TD = TT + TAPD + \frac{T}{2} \quad (5.7)$$

Where: *CPC* is predicted peak concentration at an intake for a short-duration spill, in ug/L; and *NUMDF* is the fraction of the conservation contaminant's concentration remaining at the water intake, based on the loss rate as provided by general decay factor and mean travel time from associated outfall to the intake.

- No-decay peak equilibrium concentration for a loading rate of 1 kg/s (EC, in ug/L), which was applied to calculate predicted peak concentrations at an intake, as shown in Eqs. (5.8), and the beginning and ending times of the decay-corrected peak concentration (TPKB and TPKD, in hr) and the spill plume's arrival and departure times at an intake are determined by Eqs. (5.9) to (5.12).

$$CEC = \frac{M \times EC \times NUMDSF}{T \times 3600} \quad (5.8)$$

$$TPKB = TT + \frac{TC}{2} \quad (5.9)$$

$$TPKE = TT + T - \frac{TC}{2} \quad (5.10)$$

$$TAPL = TT - TAPD \quad (5.11)$$

$$TDPL = TT + TAPD + T \quad (5.12)$$

Where: *CEC* is predicted peak concentration at an intake for a long-duration spill, in ug/L.

The input data required in the EMMCS model include the location of outfalls from which a spill enters the St Clair River, the location of the WTP intakes which may be affected by the spill, the type of spilled contaminant, total spilled mass (M, in kg), spill duration time (the length of time over which the spill occurred), an estimate of the total river flow rate at the time of the spill, and the decay characteristics of the spill. The SpillMan model also defines that: (1) the spill is a short-duration spill when the actual spill duration time (T) is shorter than the TC, and vice-versa for a long-duration spill (T > TC); (2) for a short-duration spill, both longitudinal and lateral dispersion will reduce the peak concentration of the spilled contaminant as it travels downstream; and (3) for a long-duration spill, only lateral dispersion will effectively reduce the peak concentration of the spilled contaminant. More details of the SpillMan model can be found in Nettleton and Hamdy (1988).

5.2.1.4 EMMCS Model Simulations

The risks of drinking water quality violations due to simulated benzene spills at the 11 WTP intakes along the River are determined using the EMMCS model (see Fig. 5.1). Since the spill

database has no information on SDT, a range from 0.01 to 24 hours was selected for the SpillMan model. If a spill were released for more than one day, it is assumed that measures must be implemented to stop the spill. This also corresponds to the EPCRA (1986) guide: a facility emergency plan must have a 24-hour emergency coordinator and an alternate 24-hour emergency coordinator. This also implies that a spill reporting system should include the collection of SDT information. Therefore, in order to investigate the implications of river flow conditions on the risks of water quality violations due to spills along the River, the following five flow scenarios are applied for the EMMCS simulations for the period 1988-2007: (1) monthly-based daily flow (regular case); (2) the lowest daily flow rate; (3) minimum monthly-based daily flow; (4) maximum monthly-based daily flow; and (5) the highest daily flow rate. The scenarios at the lowest daily flow rate and the highest daily flow rate are developed to provide upper and lower bounds of the risks of water quality violations, the regular case is conducted for the purpose of spill management decision-making, and the scenarios at the minimum and maximum monthly-based daily flow are to provide the range of fluctuations in the risks.

The EMMCS model also applies the MATLAB functions “RAND”, “RANDINT”, “LOGNRND”, and “WBLRND” to generate random variables by NAICS code, an industry from a NAICS group classed as a NAICS code, spilled mass, monthly based river flow rates, and minimum/maximum monthly based daily flow rates. The variable inter-event time is determined by “ $\lambda * ((\log(1/U))^{(1/\beta)})$ ” through a generated random number “ U ”. Generally, the number of simulation runs has a direct effect on the accuracy of simulation results. It is important to determine the appropriate number of simulation runs for the simulation of probabilistic spill events and time period. A 10-year simulation time period (TP) with 10^5 simulation runs that was

determined in Section 4.2.3.1 for simulating the probabilistic quantifiable occurrences of benzene spills in the River AOC were also used in the EMMCS model simulations.

In order to increase the accuracy of simulation results, the following two conditions were used in the case of daily flow rate to analyze the risk of violating drinking water quality requirements: (1) a river flow rate of 6,050 m^3/s that is the average of 6,800 and 5,300 m^3/s assumed in the SpillMan model and (2) a river flow rate of 4,921 m^3/s that is the average of 4,542 - the mean monthly minimum river flow rate during the period of 1988-2007 and 5,300 m^3/s . In terms of the river flow rate of 4,542 m^3/s , its tables of TT, TC, General Decay Factors for different values of TT, PC, and EC were obtained from those in the SpillMan model using linear interpolation. When performing EMMCSs, if a randomly-generated flow rate was greater than or equal to 6,050 m^3/s , the tables under the condition of the flow rate 6,800 m^3/s were applied; if it was smaller than or equals to 4,921 m^3/s , the tables under the condition of the flow rate 4,542 m^3/s were applied; and if it was between these two values, the tables under the condition of the flow rate 5,300 m^3/s were applied. For each simulated spill occurrence, the peak concentrations at the WTP intakes along the River were computed using the SpillMan model and compared to the benzene MAC in drinking water - 0.005 $mg L^{-1}$. The total number of simulated occurrences and the violation-causing occurrences in which the peak concentrations were greater than the MAC were then statistically analyzed.

5.2.1.5 Simulation Results and Discussion

For the regular case, the simulation spill time series that were obtained in Chapter 4 are summarized in Table 5.2. The average annual spill occurrence rates are 0.51, 0.12, 0.22, and 0.23

for the NAICSs 325210, 324110, 325110, and Unknown. The NAICS-based probabilities of drinking water quality violation are computed using Eq. (5.1) and the associated overall probabilities of violation are determined using Eq. (5.3) due to the statistical independence of the NAICS groups. The expected violation-causing occurrences at Ontario's WTP intakes for a 10-year period are between 0.3 and 1.4, while the overall probabilities (i.e. risk) of drinking water quality violation due to the simulated benzene spills are between 9 and 37%, as also indicated in Table 5.2. The simulated benzene spills from the NAICS 325210 industry group may lead to the highest risk of violation at each WTP intake followed by those from the NAICSs 324110 and 325110. The exception exists at the intake Stage Island, where the risk of violation due to the NAICS 325210 spills is lower than that of the NAICS 324110 spills. Meanwhile, Table 5.3 presents expected arrival and departure times of peak concentration and expected arrival and departure times of the spill plume at the Ontario WTP intakes, which could provide assistance to downstream WTP operators' for water quality control.

Table 5.2: Simulation benzene spill time series over 10 years in the St. Clair River AOC and expected violation-causing occurrences, NAICS-based probabilities and their overall probabilities of drinking water quality violation at the Ontario's water treatment plant (WTP) intakes from upstream to downstream along the River for month-based daily flow case (10^5 of simulation runs and [0.01, 24] hrs of spill duration time).

NAICS	325210	324110	325110	Unknown	Total
Mean Simulated Occurrence Time (Day)	1817	1573	1834	1758	-
Mean Simulated Spilled Mass (Kg)	126	687	26	15	854
Simulated Occurrences	5.1	1.2	2.2	2.3	10.8
WTP Intakes	Expected Violation-causing Occurrences				Total
Stag Island	0.2	0.1	0	0	0.3
Lambton Generating Station	1.0	0.2	0.1	0.1	1.4
Fawn Island	0.6	0.1	0.1	0	0.8
Head of Chenal Ecarte	0.7	0.2	0.1	0	1.0
Walpole Island	0.7	0.2	0.1	0	1.0
Wallaceburg	0.7	0.1	0.1	0	0.9
WTP Intakes	Probability of Violation (%)				Overall Probability (%)
Stag Island	3.9	5.1	0.3	0.2	9.2
Lambton Generating Station	19.7	15.3	5.1	2.9	37.3
Fawn Island	11.5	10.8	2.4	0.9	23.6
Head of Chenal Ecarte	14.3	12.4	3.3	1.4	28.3
Walpole Island	13.9	12.3	3.1	1.2	27.6
Wallaceburg	13.6	12.1	3.0	1.2	27.2

Table 5.3: Expected beginning and ending time of peak concentration (TPKB and TPKB) and spill plume's arrival and departure times (TAPL and TDPL) at the Ontario's water treatment plant (WTP) intakes (in hours).

NAICS	WTP Intakes	Stag Island	Lambton Generating Station	Fawn Island	Head of Chenal Ecarte	Walpole Island	Wallaceburg
325210	TPKB	3.0	7.0	11.3	14.0	15.8	23.3
	TPKB	16.4	20.2	24.3	26.8	28.5	36.2
	TAPL	1.7	5.0	8.9	11.0	12.6	15.6
	TDPL	17.6	22.1	26.8	29.8	31.7	43.9
324110	TPKB	2.7	6.5	10.7	13.5	15.2	22.8
	TPKB	14.9	18.4	22.5	25.2	26.8	34.5
	TAPL	1.7	4.8	8.4	10.8	12.3	15.4
	TDPL	1.7	4.8	8.4	10.8	12.3	15.4
325110	TPKB	1.9	5.7	9.8	12.4	13.9	21.4
	TPKB	17.8	21.4	25.3	27.7	29.2	36.8
	TAPL	1.0	4.0	7.6	9.7	11.1	14.2
	TDPL	18.8	23.1	27.6	30.4	32.1	44.0
Unknown	TPKB	0.0	2.9	7.0	9.8	11.6	19.1
	TPKB	9.9	12.4	15.5	17.9	19.4	26.3
	TAPL	0.0	1.6	5.0	7.4	8.8	12.0
	TDPL	9.9	13.7	18.2	21.2	23.3	35.2

As discussed in Chapter 4, the NAICS-based probabilities of having a specific number of inland occurrences can be determined by normal distribution function. After examining the simulated violation-causing occurrences at the WTP intakes, it is found that they could be described by exponential distributions. Their distribution parameters (μ , σ) or λ are presented in Table 5.3. Therefore, the probability of having a specific violation-causing occurrence can be estimated. As

an example, the probabilities of having one violation-causing occurrence at the WTP intakes are computed as also shown in Table 5.4. It is also observed that sources classed as NAICS 325110 would pose the highest risk of water quality violation at each intake. Fig. 5.3 illustrates the histograms of the simulated NAICS-based benzene occurrences in the River AOC and the associated violation-causing occurrences at the Ontario's WTP intakes for a 10-year period. The simulated expected values (i.e. probabilistic quantifiable occurrence of benzene spills and associated risks of drinking water quality violations at the WTP intakes along the River), as shown in Table 5.4, can provide information to both relevant industries and governments for developing spill management plans.

Table 5.4: Exponential distribution parameters for violation-causing occurrences and computed probability of one violation-causing spill occurrence in a 10-year time period at the Ontario's WTP intakes.

NAICS	325210	324110	325110	Unknown
WTP Intake	Expon. Parameter (λ)			
Stag Island	0.198	0.071	0.066	0.004
Lambton Generating Station	0.994	0.213	0.114	0.068
Fawn Island	0.58	0.151	0.007	0.022
Head of Chenal Ecarte	0.723	0.173	0.071	0.032
Walpole Island	0.712	0.171	0.068	0.029
Wallaceburg	0.686	0.168	0.068	0.029
WTP Intake	Probability of One Violation-Causing Spill Occurrences (%)			
Stag Island	18.0	6.9	6.4	0.4
Lambton Generating Station	63.0	19.2	10.8	6.6
Fawn Island	44.0	14.0	0.7	2.2
Head of Chenal Ecarte	51.5	15.9	6.9	3.1
Walpole Island	50.9	15.7	6.6	2.9
Wallaceburg	49.6	15.5	6.6	2.9

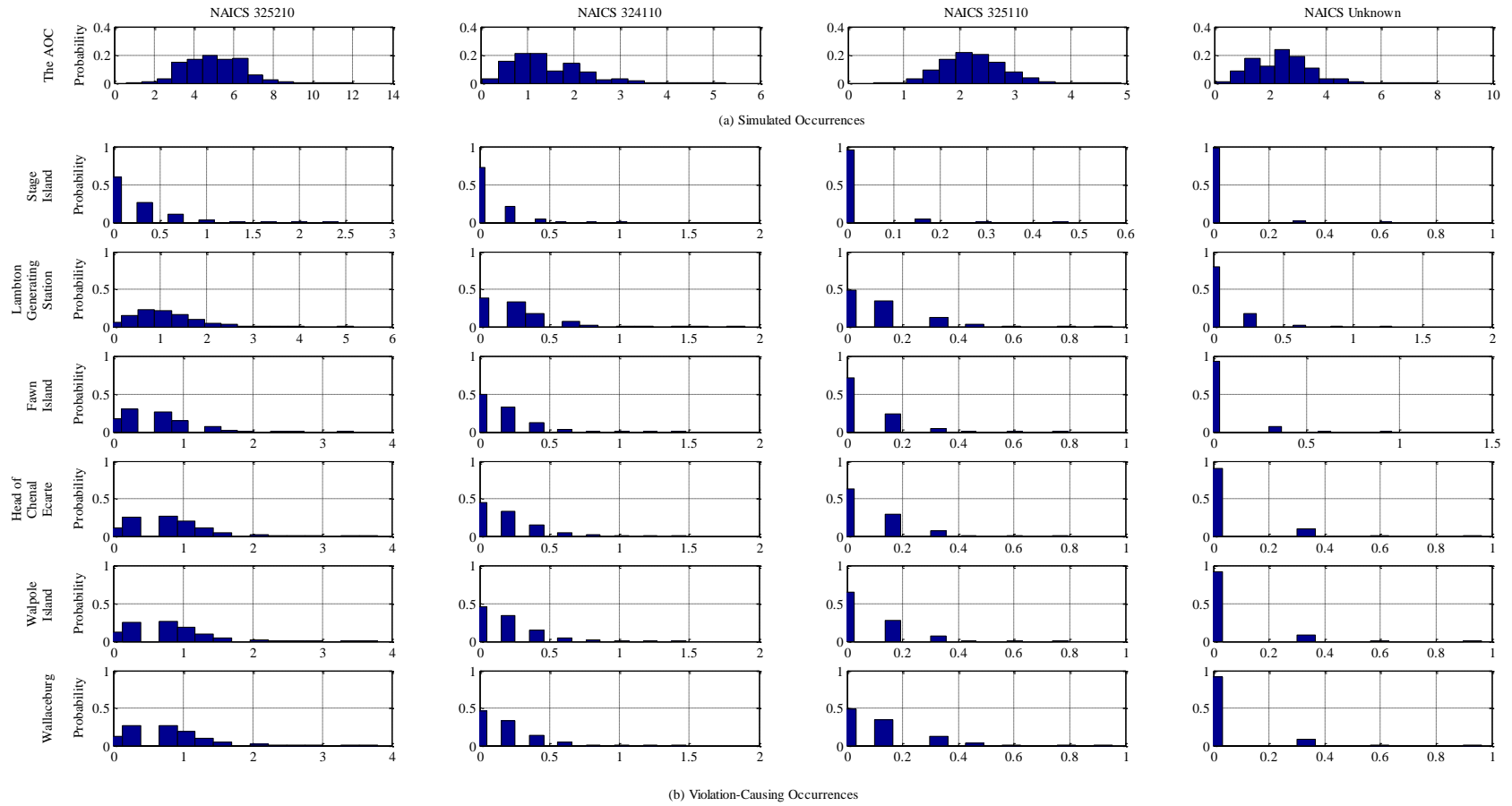


Fig. 5.3: Histograms of (a) simulated occurrences for a 10-year time period in the St. Clair River AOC and (b) violation-causing occurrences in the WTP intakes on Ontario side (10^5 simulation runs and [0.01, 24] hrs of spill duration time).

The mean violated peak concentration profiles of simulated NAICS based benzene spills at the Ontario's WTP intakes are illustrated in Fig. 5.4. The expected violated peak concentrations based on the NAICS 324110 spill are much higher than others, implying that the industries of NAICS 324110 should pay attention to spill prevention and control. It is observed that the mean violated peak concentrations decrease from upstream to downstream except the three intakes at Stag Island, Fawn Island, and Walpole Island where the concentrations are lower than those of their downstream intakes. This may be attributed to the three islands on the other side of the River where lateral advection, dispersion, and diffusion could cause great effects on the transport of the spills leading to relatively lower concentrations there. Although the intake at Stag Island has the shortest distance from the spill causing industries, it is located farther away from the river bank where lateral advection, dispersion and diffusion may be more pronounced than near the shore. SpillMan model could be easily to recognize these conditions through its tables created from the Ontario MOE's actual project results.

For the other 4 limiting scenarios that were conducted under the flow conditions of the highest daily flow, maximum month-based daily flow, minimum month-based daily flow, and the lowest daily flow, the overall probabilities of drinking water quality violation at Ontario's WTP intakes are compared in Fig. 5.5. The maximum overall probabilities of violation fluctuate between 31.7 and 39.5%. No violation-causing occurrence is found at the intakes on the Michigan side except the intake at Old Club, which may be attributed to the same reasons as those of the intakes at Ontario's three islands. At the intake at Old Club, the NAICSs 325210 and 324110 caused water quality violation with the probabilities of 0.7 and 4.6% and expected peak concentrations of 0.01 and 0.07 mg/L over a 10-year period. This may be attributed to the fact

that the mean spilled masses of NAICSs 325210 and 324110 were much high (due to a spill event with much high mass in each of them) and the Old Club intake is located at a branch of the St Clair River where flow rate was lower than main stream resulting water quality violation. However, the violation-causing occurrences at the Old Club intakes were found to be lower than other intakes. Therefore, it could be concluded that the simulated benzene spills would not impair the drinking water quality at the Michigan intakes but further research on extreme spill events should be conducted to investigate water quality violation at all intakes.

5.2.1.6 Uncertainty Analysis

Uncertainty analysis was conducted under the flow condition of month-based daily flow. A bootstrap resample using EMMCS was repeated one thousand times to determine the uncertainty of the spill related distributional parameters. The uncertainty of river flowrate related distributional parameters was not analyzed due to sufficient flow data of the river provided by Environment Canada. For each simulation of the EMMCSs, a subset of benzene spill inter-event time and spilled mass was first generated using the nonparametric unbalanced bootstrapping technique for each NAICS code. Similar to the PDs of the original NAICS codes, the PDs of these bootstrap subsets (i.e. inter-event time and spilled mass) followed Weibull and lognormal distributions. The PDs' parameters were then estimated using the maximum likelihood method. After performing 1000 simulations of EMMCS, the spill occurrence, the mean spill occurrence time, the mean spilled mass in the River AOC, and the violation-causing occurrences at the WTP intakes over the next 10 years were determined. It was found that the lognormal distribution could properly describe the PDs of NAICS-based simulated spill occurrences, the mean spill occurrence, and the mean spilled mass of each NAICS code.

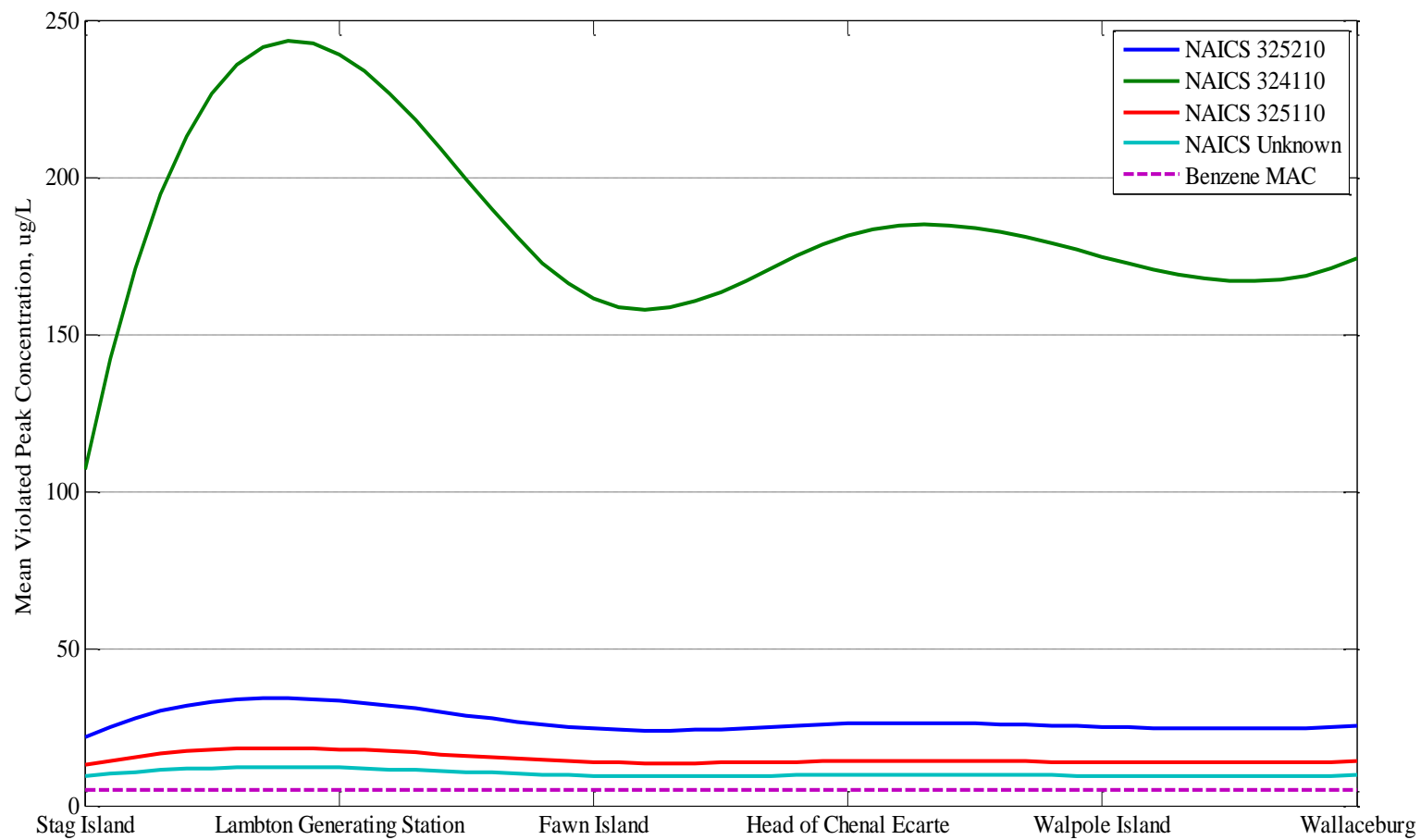


Fig. 5.4: NAICS-based mean violated peak concentration profile of simulated benzene spills at the Ontario's water treatment plant intakes along the St. Clair River.

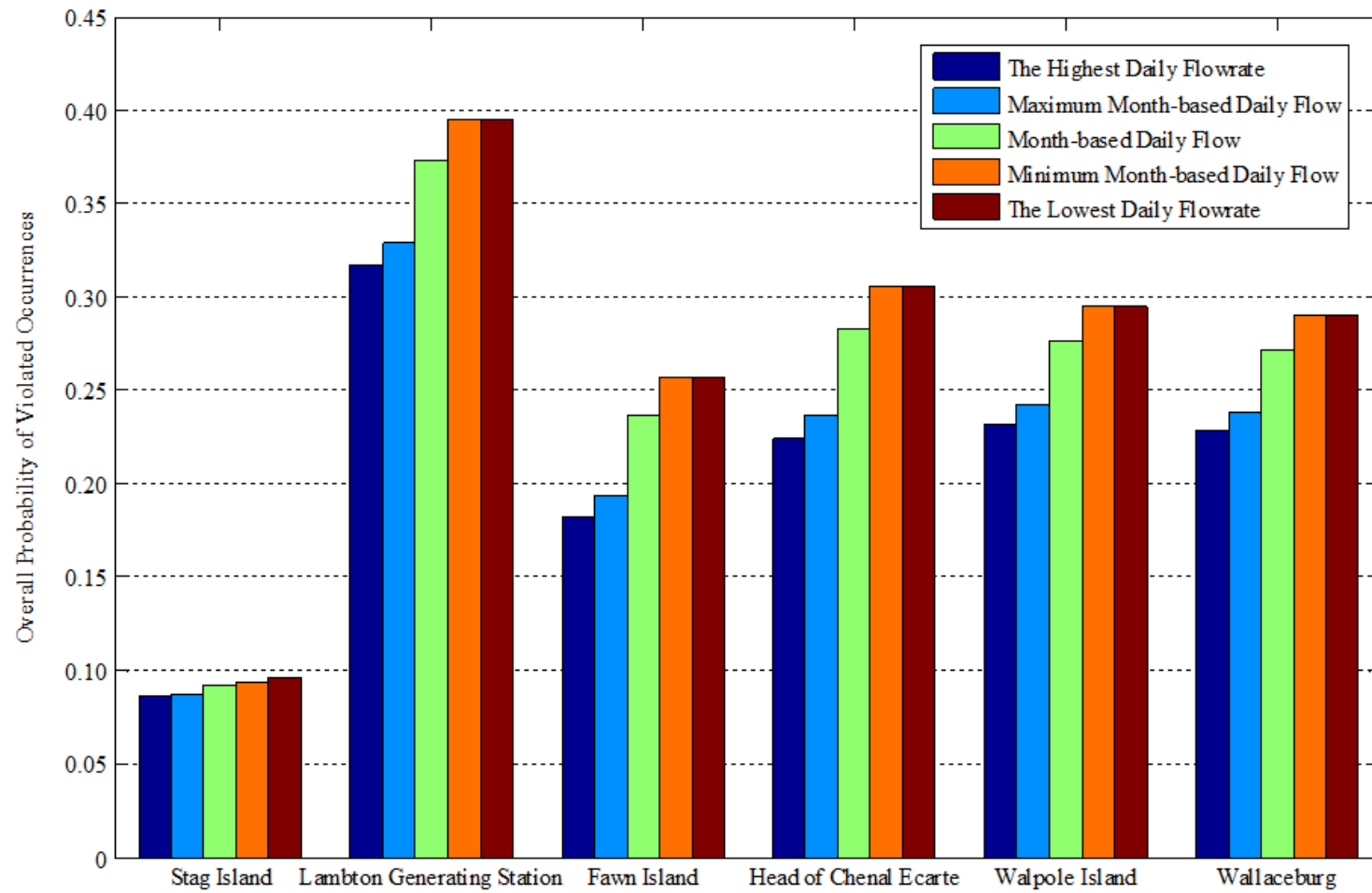


Fig. 5.5: Comparison of overall probabilities of violation-causing occurrences at the water treatment plant intakes along the St Clair River on the Ontario side at various scenarios.

The sample mean, standard deviation, and 95% confidence interval of NAICS-based and overall probabilities of drinking water quality violation at the WTP intakes on the Ontario side are presented in Table 5.5 presents. In addition, the NAICS-based probabilities of drinking water quality violation are observed to be Weibull distributed. Fig. 5.6 illustrates their histograms and Weibull distributions.

Table 5.5: Bootstrapped resampling statistics of NAICS-based and overall probabilities (Prob.) of drinking water quality violation at the Ontario's water treatment plant (WTP) intakes for month-based daily flow case (10^5 of simulation runs, [0.01, 24] hrs of spill duration time, and 10 yrs of simulation time period).

WTP Intakes	NAICS Code	Mean	St. Dev.	95% Confidence Interval	
				Lower Bound	Upper Bound
Stag Island	325210	0.029	0.015	0.028	0.030
	324110	0.028	0.025	0.027	0.030
	325110	0.002	0.002	0.002	0.002
	Unknown	0.002	0.001	0.002	0.002
	Overall Prob.	0.060	0.029	0.058	0.061
Lambton Generating Station	325210	0.167	0.060	0.163	0.170
	324110	0.102	0.065	0.098	0.106
	325110	0.037	0.025	0.035	0.038
	Unknown	0.026	0.011	0.025	0.026
	Overall Prob.	0.297	0.076	0.293	0.302
Fawn Island	325210	0.090	0.040	0.087	0.092
	324110	0.066	0.050	0.063	0.069
	325110	0.015	0.015	0.014	0.016
	Unknown	0.008	0.005	0.007	0.008
	Overall Prob.	0.168	0.060	0.165	0.172

Table 5.5 (cont'd)

WTP Intakes	NAICS Code	Mean	St. Dev.	95% Confidence Interval	
				Lower Bound	Upper Bound
Head of Chenal Ecarte	325210	0.115	0.048	0.112	0.118
	324110	0.078	0.056	0.074	0.081
	325110	0.020	0.019	0.019	0.021
	Unknown	0.011	0.007	0.011	0.012
	Overall Prob.	0.209	0.068	0.205	0.214
Walpole Island	325210	0.111	0.048	0.108	0.114
	324110	0.076	0.056	0.073	0.080
	325110	0.019	0.019	0.018	0.020
	Unknown	0.010	0.006	0.009	0.010
	Overall Prob.	0.202	0.068	0.198	0.206
Wallaceburg	325210	0.108	0.047	0.106	0.111
	324110	0.075	0.055	0.072	0.078
	325110	0.019	0.018	0.017	0.020
	Unknown	0.010	0.006	0.009	0.010
	Overall Prob.	0.199	0.066	0.195	0.203

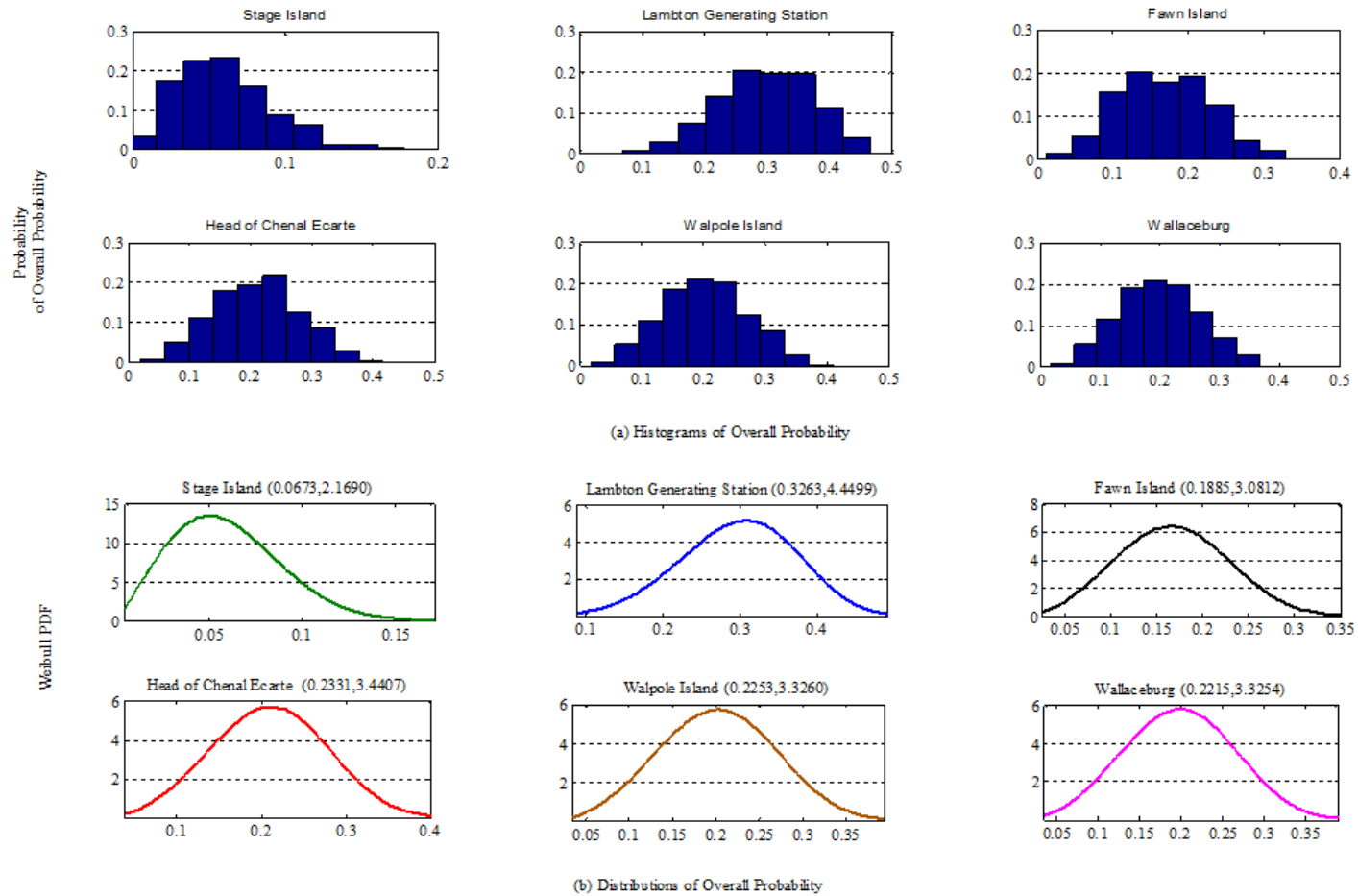


Fig. 5.6: Histograms and Weibull distributions of overall probabilities of drinking water quality violation due to simulated benzene spills at the Ontario's water treatment plant intakes along the St. Clair River for month-based daily flow case (1000 bootstrapped replications, 10^5 of simulation runs, [0.01, 24] hrs of spill duration time, and 10 yrs of simulation time period).

5.2.2 Risks of Drinking Water Quality Violation due to Benzene Spills along Mimico Creek

5.2.2.1 Background of Mimico Creek

Mimico Creek is a tributary of Lake Ontario, which starts in the City of Brampton and flows through the City of Mississauga and the City of Toronto in the Greater Toronto Area (GTA) of Ontario, Canada, and drains into Lake Ontario (TRCA_a). It is 32 kilometers in length and has a total drop in elevation of 160 meters (The Region of Peel). As Toronto Region Conservation Authority reported, the Mimico Creek watershed is highly urbanized and degraded systems (TRCA, 2010), resulting in a “flashy” response to rainfall events (TRCA_a). When rain falls on the ground, it travels overland and reaches the watercourse quickly. It is a long, narrow and relatively steep watershed with a total area of approximately 77 km². Water quality is generally poor and there is a low diversity of aquatic and terrestrial habitats. Only 5 km² comprise parks, conservation areas and trails that provide important opportunities for recreation, wildlife and habitat restoration. “As the watershed is shaped so extensively by human intervention, its management requires close attention to the protection, enhancement and expansion of its remaining natural systems and the improvement of its water quality by improving and limiting urban storm water runoff” (TRCA_b).

5.2.2.2 Correlations and Probability Distributions of EMMCS Model Variables

The potential spill inter-event time, occurrence times, spilled mass, and daily river flowrates

were assumed to be statistically independent of each other according to the case study of benzene spills in the St Clair River AOC. The PDs of the NAICS-based benzene spill inter-event time (Weibull distribution) and spilled mass (lognormal distribution) obtained for the case of the Mimico Creek watershed in Chapter 4 are applied for investigating water quality violations in compliance with the benzene MAC in drinking water at selected downstream locations along Mimico Creek. Flow information on Mimico Creek for the period 1988-2007 was retrieved from Environment Canada HYDAT Database (Environmental Canada). Using a maximum likelihood estimator to test various distributions, including normal, lognormal, Weibull, exponential, and Gamma, for the goodness-of-fit for the PDs of the month-based daily flowrates of Mimico Creek, it is found that they could be properly described by lognormal distributions. Fig. 5.7 illustrates their fitted CDFs and Table 5.5 summarizes their parameters. As shown in Table 5.6, all parameter μ_y values are negative because of the negative skewness of the distributions.

Table 5.6: Estimated parameters of the lognormal distributions of month-based daily flowrates in the Mimico Creek by using MATLAB functions.

Month	μ_y	σ_y	Month	μ_y	σ_y
Jan	-1.0743	1.1379	Jul	-1.2268	1.1647
Feb	-0.8611	1.0674	Aug	-1.4077	1.2282
Mar	-0.4520	0.9310	Sept	-1.3553	1.2067
Apr	-0.4714	0.9647	Oct	-1.2788	1.1287
May	-0.7800	1.0490	Nov	-0.9473	1.2087
Jun	-1.0434	1.1036	Dec	-0.9988	1.0363

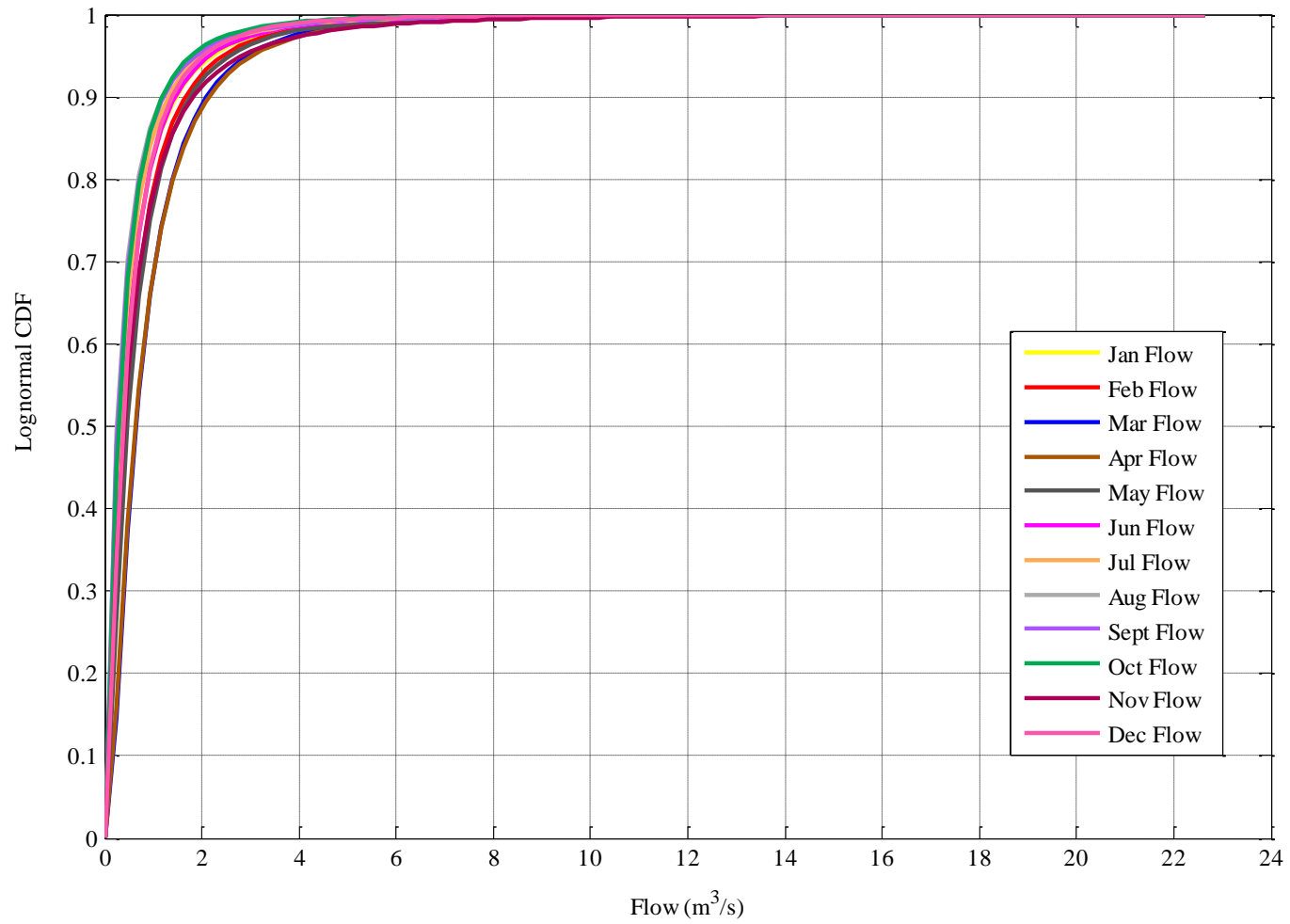


Fig. 5.7: Fitted lognormal cumulative month-based daily flow rates in the Mimico Creek.

5.2.2.3 Water Quality Model

As introduced above, Mimico Creek is a long and narrow creek with low flow rate and relatively steep watershed. Therefore, the creek can be considered as a small river differencing from a large river because the former together with streams becomes the latter. According to Neely *et al.*'s (1976), a river may be visualized as a series of continuous stirred flow compartments to the first approximation. In terms of the fate of benzene in Mimico Creek, although water dispersion will affect the concentrations of a benzene spill at the downstream locations along the creek, this effect can be considered as small since the creek is a narrow small river. Once benzene enters into the creek, it will mix with the water immediately and reach the other side of the creek quickly. Therefore, Mimico Creek can be treated as a series of n continuous stirred flow compartments and the water quality model for benzene spills along Mimico Creek is developed based on Neely *et al.*'s (1976) Eqs. (2.20) to (2.22). The mass balance for benzene spill through the n th compartment is given by Eq. (5. 13).

$$\frac{VdC_n}{dt} = I - O - G - F - B - P - S \quad (5.13)$$

where:

- C_n is the spill concentration in the n th compartment, kg/m^3 ;
- V is the volume of the n th compartment, m^3 ;
- t is time, s ;
- I is mass rate entering into the n th compartment, kg/s , which is calculated as QC_{n-1} , where Q is river flowrate (m^3/s) and C_{n-1} is concentration in the $(n-1)$ th compartment;

- O is mass rate leaving the n th compartment, kg/s , which is calculated as QC_n ;
- G is mass loss rate due to water-to-air exchange, kg/s , which is determined by $k_e AC_n$ (Wick *et al.*, 2000), where k_e is the exchange rate of water-to-air that is 0.5 m/d (Schwarzenbach *et al.*, 1993) and A is surface area of the compartment (m^2);
- B is mass loss rate due to biodegradation, kg/s , which is considered as the pseudo-first-order decay and so can be determined by $k_b VC_n$, where k_b is decay rate that is between 1 and 2.5 per day (Wick *et al.*, 2000) and 1.5 per day is used in this study;
- F is mass loss rate due to episodic flushing events, kg/s , which can be negligible because only large rain events will affect this loss and it is difficult to quantify it in these event (Wick *et al.*, 2000);
- P is mass loss rate due to photolysis, kg/s , which can be negligible since benzene does not undergo a significant direct photolysis in sunlight (Wick *et al.*, 2000).
- S is the mass loss rate due to settlement, kg/s , which can be negligible due to a very low loss of benzene to the sediment bed (Wick *et al.*, 2000).

Therefore, the mass balance Eq. (5.13) can be simplified to Eq. (5.14) by using the expressions of I , Q , G , and B and neglecting F , P and S .

$$\frac{VdC_n}{dt} = Q(C_{n-1} - C_n) - k_e AC_n - k_b VC_n \quad (5.14)$$

In the first compartment $C_1(0) = M/V_1$, where M is spilled mass entered river instantaneously at time $t = 0$. The concentration of chemical for all compartments other than the first ($n \geq 2$) initially is set to be $C_n(0) = 0$. Solving the differential Eq. (5.14), the concentration in the n th

compartment at time t can be determined by Eq. (5.15). Setting the derivative of the right-hand side of Eq. (5.15) to zero, the time for the maximum concentration to reach any point downstream is obtained, as expressed by Eq. (5.16). Substituting Eq. (5.16) for t in Eq. (5.15) and involving Stirling approximation, $n! \approx \sqrt{2\pi n} \left(\frac{n}{e}\right)^n$, the corresponding maximum concentration can be determined by Eq. (5.17). To apply these equations, it is assumed that benzene concentration is homogeneous in each compartment and no water dispersion effect on the concentration.

$$C_n(t) = \frac{M \left(\frac{Q}{V} t \right)^{n-1}}{V(n-1)!} \exp \left(- \left(\frac{k_e}{h} + k_b + \frac{Q}{V} \right) t \right) \quad (5.15)$$

$$t_{n, \max} = \frac{n-1}{\frac{k_e}{h} + k_b + \frac{Q}{V}} \quad (5.16)$$

$$C_{n, \max} = \frac{M}{V} \left(\frac{\frac{Q}{V}}{\frac{k_e}{h} + k_b + \frac{Q}{V}} \right)^{n-1} \frac{1}{\sqrt{2\pi(n-1)}} \quad (5.17)$$

Compared to Eqs. (2.20) to (2.22), Eqs. (5.15) to (5.17) are similar to them except for involving decay rate k_b . Usually, to develop a water quality model for a specific pollutant starts with a mass balance that consists of all impact factors and then simplifies it according to the physical, biological, or chemical characteristics of the pollutant before solving the mass balance equation.

5.2.2.4 EMMCS Model Simulations

If continuous data on river width and depth are lacking on a global scale (Schulze *et al.*, 2005), the river width and depth can be estimated as a function of channel discharge, as expressed in Eqs. (5.18) and (5.19) introduced by Leopold and Maddock (1953). Their applications can be found in hydrology textbooks (e.g. Mosley and McKerchar, 1993; Dunne and Leopold, 1978). In order to quantify the best-fit coefficients (a and b) and exponents (c and f) in Eqs. (5.20) and (5.21), Allen *et al.* (1984) obtained their values through conducting a regression analysis with a dataset of 674 river cross sections across the U.S. and Canada. The 0.88 and 0.75 of coefficients of determination (R^2) were presented for width and depth, respectively. The values of a , b , c , f were valid for bankfull discharge (Q_b), which were used for this case study. Therefore, Eqs. (5.16) and (5.17) become Eqs. (5.20) and (5.21). In the case of Mimico Creek, it is assumed that the hydraulic radius of a non-bankfull river follow the geometric rules as bankfull discharge. As no information pertaining to the width and depth of the creek is available, Eqs. (5.20) and (5.21) are used to model the width and depth of the creek during the EMMCS simulations. For a selected length, L , of each compartment, the volume can be calculated as Eq. (5.22).

$$W = aQ^b \quad (5.18)$$

$$D = cQ^f \quad (5.19)$$

$$W = 2.71Q_b^{0.557} \quad (5.20)$$

$$D = 0.349Q_b^{0.341} \quad (5.21)$$

$$V = W \cdot D \cdot L \quad (5.22)$$

The potential benzene spill time series in the Mimico Creek watershed are simulated for various

scenarios of 0.1, 1, 5, and 10 *m* length of each compartment for the purpose of investigating the implications of the length of compartments on the risks of drinking water quality violation due to simulated spills at downstream locations. Following the St Clair River case, the [0.01, 24] hours range of spill duration time SDT, 10-year simulation time period (TP), and 10^5 simulation runs are used in this case. The EMMCS simulations are based on seven potential industries with representatives of NAICS codes, whose locations are shown in Fig. 4.7. The values of the distances from the industries to the outlets to the creek and from the upstream outfalls to the downstream mouth at Lake Ontario are measured by using ArcGIS software. By using a 2 *m/s* of mean velocity in a sanitary sewer (City of Mississauga, 2009), the travel times between spill locations and the outlets to the creek are then estimated. Table 5.7 presents the information on inland travel distances and travel times and distances between selected locations along Mimico Creek and the mouth of Lake Ontario. As shown in the table, most travel times are shorter than 3.1 minutes except for one industry with 10 minutes. Therefore, the inland decay of benzene is assumed to be neglected, resulting in all simulated benzene masses entering into Mimico Creek. Similar to the inland benzene spill simulations in the Mimico Creek watershed in Chapter 4, the uncertainty analysis for the parameters of the PDs of inter-event times and spilled masses are not conducted.

Table 5.7: NAICS-based inland distances and travel times to the Mimico Creek, and distances between outfalls and the mouth of the Lake Ontario.

Potential NAICS Industry	N325210-11	N325210-12	N325210-13	N325110-21	N325110-22	N324110-31	N324110-32
Inland Travel Distance to Entrance Measured by ArcGIS (m)	260	104	1205	295	246	368	165
Inland Travel Time to Entrance (min)	2.2	0.9	10.0	2.5	2.1	3.1	1.4
Selected Location	Distance away from mouth (km)						
	Entrance						
Location 19	-	-	-	29.0	-	26.6	-
Location 18	-	-	-	28.5	-	26.4	-
Location 17	-	-	-	28.0	-	26.2	-
Location 16	-	-	-	27.5	-	25.8	-
Location 15	-	-	-	27.0	-	25.6	-
Location 14	24.4	-	-	26.5	-	25.4	24.0
Location 13	24.2	-	-	26.0	-	25.0	23.9
Location 12	23.9	-	-	24.5	-	24.2	23.8
Location 11	23.7	-	-	23.9	-	23.7	23.7
Location 10	23.3	-	-	23.4	-	23.3	23.3
Location 9	22.9	-	-	22.9	-	22.9	22.9
Location 8	22.7	-	-	22.7	-	22.7	22.7
Location 7	22.2	-	-	22.2	-	22.2	22.2
Location 6/Main Stream Starting Here	21.8	19.6	19.6	21.8	17.3	21.8	21.8
Location 5	17.3	17.3	17.3	17.3	15.3	17.3	17.3
Location 4	13.3	13.3	13.3	13.3	13.3	13.3	13.3
Location 3	9.3	9.3	9.3	9.3	9.3	9.3	9.3
Location 2	5.3	5.3	5.3	5.3	5.3	5.3	5.3
Location 1	2.3	2.3	2.3	2.3	2.3	2.3	2.3
Location 0/Mouth of Lake Ontario)	0	0	0	0	0	0	0

5.2.2.5 Simulation Results and Discussion

Under simulation conditions (i.e., [0.01, 24] hours of SDT, 10 years of TP, and 10^5 simulation runs), the scenarios of 0.1, 1, 5, and 10 m length of each compartment were conducted. The industries' concentration profiles related to distance and associated arriving time along Mimico Creek are shown in Fig 5.8 (a) and (b), while their probabilities (i.e. risks) of drinking water quality violation caused by each industry at the downstream location are illustrated in Fig. 5.9. As observed in these figures, the peak concentrations and violation probabilities reduced quickly to much lower values after travelling a few kilometers from outfall to downstream. The shorter the length of each compartment leading to a smaller volume, the lower the downstream peak concentrations and violation probabilities, as revealed by Eq. (5.17) having been applied to this case (i.e. treating a small river as a series of compartments and the concentration in each compartment assumed to be same).

In addition, in order to investigate the effect of benzene decay rate k_b on the annual occurrences and risks of water quality violation at the downstream locations, the simulations are also conducted respectively using 1 (minimum rate by Wick *et al.*, 2000) and 2.5 (maximum rate Wick *et al.*, 2000) day^{-1} of biodegradable rates with 10 m length of each compartment. It is found that most annual occurrences and risks of water quality violation at the same location from the same industry are same under the decay rates of 1, 1.5, and 2.5 day^{-1} . The maximum differences of annual occurrence and risk are 0.003 and 0.015 respectively. It can be concluded that the change of benzene decay rate has very small effect on the risks of water quality violation and can be neglected. Therefore, the length of each compartment becomes a control factor for the decay of spill concentration. Although there are no direct field data available for calibrating the water

quality model, it would be reasonable to apply the simulation results of the EMMCS model for the purpose of spill prevention and management.

The NAICS-based and City-based expected annual benzene spill occurrences and violation-causing occurrences (including those at the entrances of Mimico Creek and some selected downstream locations along its length) in compliance with 0.005 *mg/L* of benzene's MAC in drinking water are summarized in Tables 5.8 and 5.9. As shown in Table 5.8, the City of Mississauga may experience the highest potential benzene spills occurrences followed by the Cities of Brampton and Toronto. For all simulation scenarios, violation-causing occurrences present very small numbers at main stream's downstream locations. It is observed that the simulated spills in the City of Brampton do not violate the benzene MAC at downstream locations close to the mouth of Lake Ontario, which may be attributed to the long distance between the outfall and the mouth. Table 5.9 suggests that the NAICS 325210 will have the highest inland potential spill occurrences and violation-causing occurrences. Similarly, very low violation-causing occurrences are seen at downstream locations. The potential spills from the NAICS 324110 industry will not violate the benzene MAC at the outlet to the creek as well at the downstream locations.

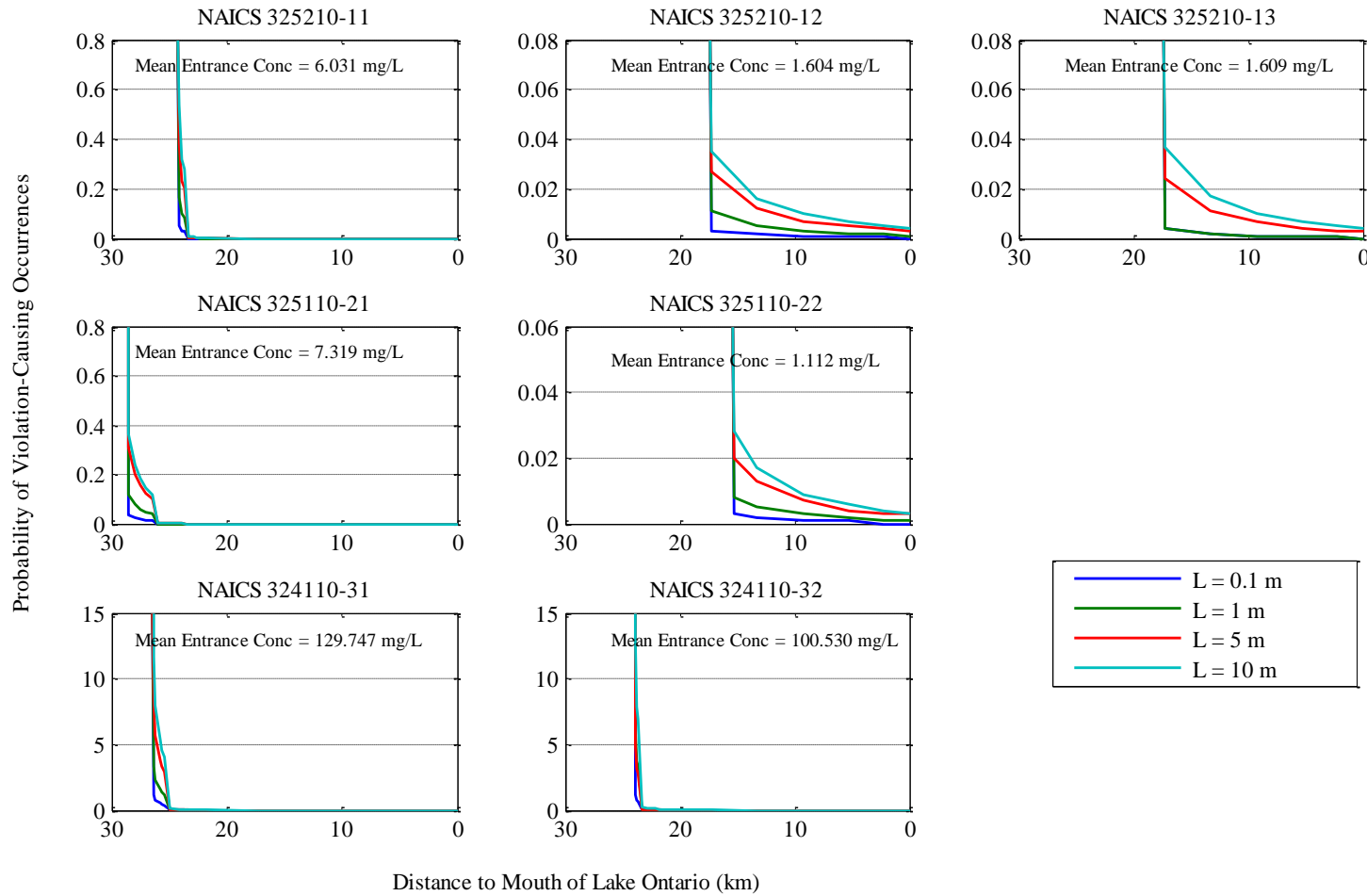


Fig. 5.8: Potential industrial benzene spill concentration profiles along the Mimico Creek (10^5 of simulation runs and [0.01, 24] hrs of spill duration time).

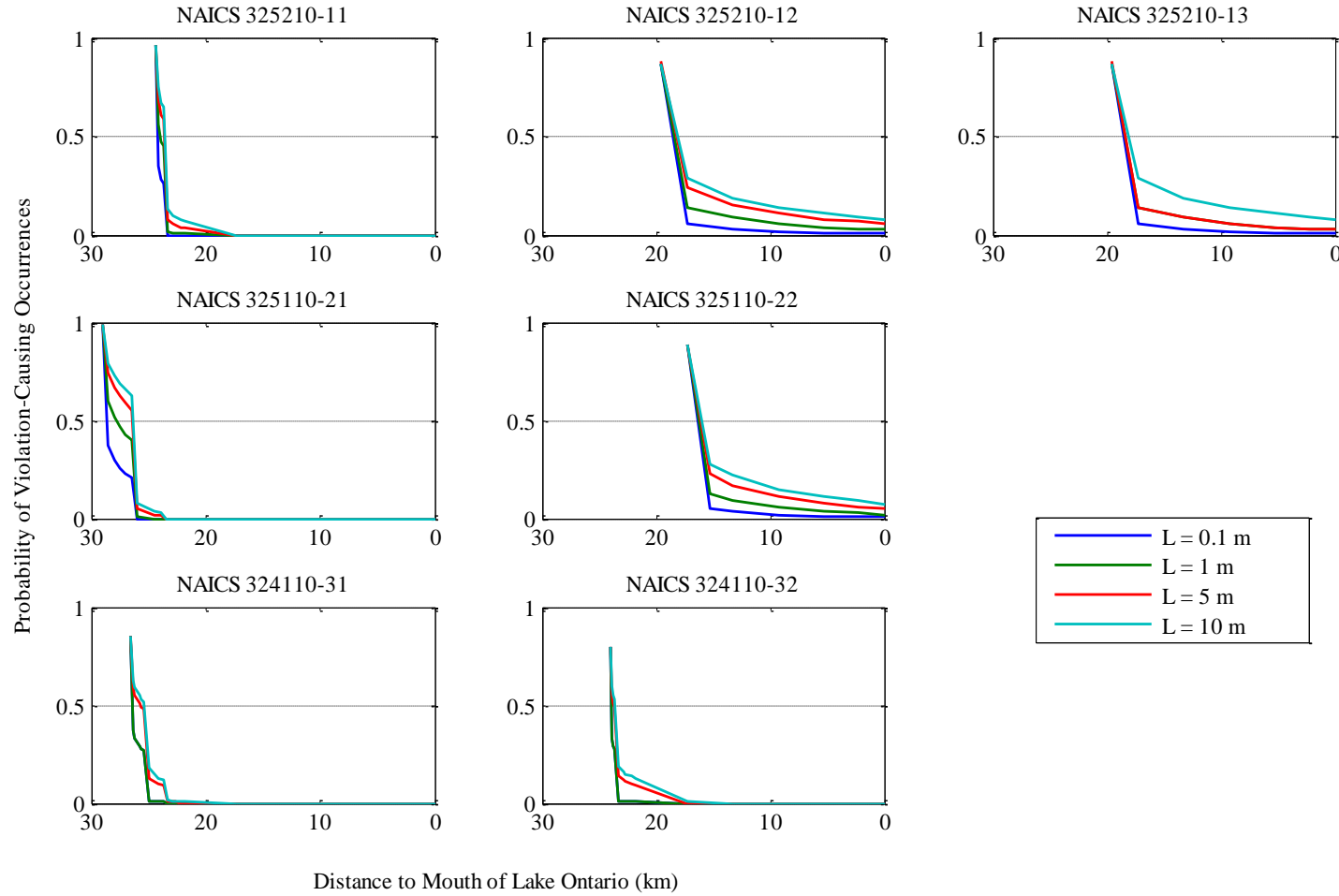


Fig. 5.9: Probabilities of drinking water quality violation caused by simulated industrial spills at the downstream location (10^5 of simulation runs and [0.01, 24] hrs of spill duration time).

Table 5.8: Comparison of expected inland total annual occurrences, inland violation-causing occurrences, and downstream violation-causing occurrences due to city-based simulated spills (10^5 simulation runs and [0.01, 24] hrs of spill duration time).

Compartment Length (m)		L = 0.1	L = 1	L = 5	L = 10
Mississauga	Total Occurrences (/yr)	0.64	0.65	0.65	0.64
	Violation-causing occurrences (/yr)	0.57	0.57	0.58	0.57
	Violation-causing occurrences (/yr) at main stream (distance from the mouth of Lake Ontario, km)				
	Location 4 (13.3)	0.01	0.03	0.06	0.07
	Location 3 (9.3)	0.01	0.02	0.04	0.05
	Location 2 (5.3)	0.01	0.02	0.03	0.04
	Location 1 (2.3)	0.00	0.01	0.02	0.03
	Location 0 (0)	0.00	0.01	0.02	0.03
Brampton	Total Occurrences (/yr)	0.22	0.22	0.22	0.22
	Violation-causing occurrences (/yr)	0.20	0.20	0.20	0.20
	Violation-causing occurrences (/yr) at main stream (distance from the mouth of Lake Ontario, km)				
	Location 4 (13.3)	0.00	0.00	0.00	0.00
	Location 3 (9.3)	0.00	0.00	0.00	0.00
	Location 2 (5.3)	0.00	0.00	0.00	0.00
	Location 1 (2.3)	0.00	0.00	0.00	0.00
	Location 0 (0)	0.00	0.00	0.00	0.00
Toronto	Total Occurrences (/yr)	0.12	0.12	0.12	0.12
	Violation-causing occurrences (/yr)	0.11	0.11	0.10	0.11
	Violation-causing occurrences (/yr) at main stream (distance from the mouth of Lake Ontario, km)				
	Location 4 (13.3)	0.00	0.01	0.02	0.03
	Location 3 (9.3)	0.00	0.01	0.01	0.02
	Location 2 (5.3)	0.00	0.00	0.01	0.01
	Location 1 (2.3)	0.00	0.00	0.01	0.01
	Location 0 (0)	0.00	0.00	0.01	0.01

Table 5.9: Comparison of expected inland total annual occurrences, inland violation-causing occurrences, and downstream violation-causing occurrences due to NAICS-based simulated spills (10^5 simulation runs and [0.01, 24] hrs of spill duration time).

Compartment Length, L (m)		L = 0.1	L = 1	L = 5	L = 10
NAICS325210	Total Occurrences (/yr)	0.54	0.55	0.55	0.54
	Violation-causing occurrences (/yr)	0.49	0.49	0.50	0.49
	Violation-causing occurrences (/yr) at main stream (distance from the mouth of Lake Ontario, km)				
	Location 4 (13.3)	0.01	0.03	0.06	0.07
	Location 3 (9.3)	0.01	0.02	0.04	0.05
	Location 2 (5.3)	0.01	0.02	0.03	0.04
	Location 1 (2.3)	0.00	0.01	0.02	0.03
	Location 0 (0)	0.00	0.01	0.02	0.03
NAICS325110	Total Occurrences (/yr)	0.24	0.24	0.23	0.24
	Violation-causing occurrences (/yr)	0.22	0.22	0.22	0.22
	Violation-causing occurrences (/yr) at main stream (distance from the mouth of Lake Ontario, km)				
	Location 4 (13.3)	0.00	0.01	0.02	0.03
	Location 3 (9.3)	0.00	0.01	0.01	0.02
	Location 2 (5.3)	0.00	0.00	0.01	0.01
	Location 1 (2.3)	0.00	0.00	0.01	0.01
	Location 0 (0)	0.00	0.00	0.01	0.01
NAICS324110	Total Occurrences (/yr)	0.20	0.20	0.20	0.20
	Violation-causing occurrences (/yr)	0.17	0.17	0.17	0.17
	Violation-causing occurrences (/yr) at main stream (distance from the mouth of Lake Ontario, km)				
	Location 4 (13.3)	0.00	0.00	0.00	0.00
	Location 3 (9.3)	0.00	0.00	0.00	0.00
	Location 2 (5.3)	0.00	0.00	0.00	0.00
	Location 1 (2.3)	0.00	0.00	0.00	0.00
	Location 0 (0)	0.00	0.00	0.00	0.00

The illustrations of the histograms of the simulated City-based benzene occurrences for a 10-year time period in the Mimico Creek watershed and associated violation-causing occurrences at some selected downstream locations are shown in Appendix A.4.1, while those of the simulated NAICS-based occurrences and associated violation-causing occurrences at selected downstream locations, for the scenario of 0.1, 1, 5, 10 *m* lengths of compartments can be found in Appendix A.4.2. As observed in all scenarios (shown in Figs. A.4.1 and A.4.2), the violation-causing occurrences in the City of Brampton by NAICS 324110 are very small at the selected downstream locations, which implies that the probabilities of water quality impairments close to the mouth of the Lake Ontario will be very small. Fig. A.4.1 also suggests that the City of Mississauga would have the highest probability to experience one inland violation-causing occurrence, while Fig. A.4.2 shows that NAICS 325210 would have the most spill occurrences. Both figures present very low probabilities to have one violation-causing occurrence close to the mouth of Lake Ontario.

5.3 Summary of Findings Regarding EMMCS Simulations

Based on the above simulation results, the following findings are summarized:

- The proposed EMMCS can simulate spill time series, including the probabilistic spill occurrences by time, magnitude, and NAICS-based location, and determine the associated quantitative risks of water quality impairments at any location downstream of receiving waters.
- The model can provide information on prior industries that could need to reduce spill frequency and magnitude by implementing spill prevention and control. Regulatory agencies and municipalities can use the model to evaluate the effectiveness of actions

against inland spills, make decisions on where to implement management measures and allocate resources.

- The simulated expected violation-causing benzene spills occurrences at the Ontario's WTP intakes are between 0.3-1.4 resulting in 9.2-37.3% of overall probabilities of drinking water quality violation in compliance with the maximum acceptable concentration in a 10-year period. No drinking water quality impairments could be concluded at the Michigan intakes.
- The simulation results of one thousand times of bootstrap resampling suggested that the NAICS-based and overall probabilities of drinking water quality violation were Weibull distributed. In terms of risk-informed decision making, the NAICS 325210 must pay attention to spill prevention and control, and emergency response onsite or downstream if a spill could not be controlled or cleaned-up.
- Cooperation and information sharing between Canada and the U.S. should be considered for the control and management of benzene spills, especially from the industries of NAICSs 325210 and 324110.
- The simulation results of benzene spills in Mimico Creek show that 99% of spilled masses have relatively small values leading to very low probabilities of having one violation-causing occurrence at the locations that are close to the mouth of Lake Ontario (about 14 km). When historical spill data are unavailable, the method of transferring available historical spill data from one area to another one with reasonable adjustments would help to provide valuable information to industries or municipalities with respect to benzene spill prevention and management.

CHAPTER 6 COMPREHENSIVE INLAND SPILL MANAGEMENT PLANNING FRAMEWORK

Inland chemical spills can be significant environmental events that potentially impair receiving water quality and damage human health. Spills in large quantity could acutely elevate certain toxic chemicals at water intakes (Cheng, 2010). Even small quantity spills could increase chronic toxicity levels in receiving waters. As discussed in Chapter 3, hundreds of chemical spills occur every year in Southern Ontario, resulting in surface water impact and other multiple environmental implications. Additionally, receiving waters have experienced continuous impairments by thousands of spilled chemicals (Cao *et al.*, 2012). According to Fig. 3.1, for the 5-year period of 2003-2007, the numbers of chemical spill events have an increasing tendency, implying that industries may not well prevent, control, and manage their spill problems. Therefore, a comprehensive inland chemical spill management framework is acutely needed to assist industries and governmental organizations to allocate considerable resources to conduct analyses and preparedness tests (Kenar *et al.*, 2007) to protect source water quality, human health and ecosystem health. CCME (2008) published a “*Canada-wide strategy for the management of municipal wastewater effluent environmental risk management framework and guidance*”, whose recommendations are very practical and helpful for spill prevention, control and management and are presented in the following sections.

However, no such framework can be found in most municipalities across Canada. A survey of municipal preparedness for spills in major cities in Canada between 2006 and 2007 indicated that

only Toronto and Edmonton had a sewer use bylaw, a spill management plan, and an emergency spill response team simultaneously (Han, 2007). Spill management plans have been reported to exist for cities such as Toronto, Edmonton and Victoria, while most cities have a sewer use bylaw and some have a spill response team. Responding to this challenge, a comprehensive chemical spill management framework is developed, which consists of a spill pollution prevention plan, a spill control plan, and an emergency response plan, as shown in Fig. 6.1 (Cao *et al.*, 2012). Through effective technical planning tools, such as the MMCS and EMMCS models proposed in Chapters 4 and 5, it would be appropriate for a municipality to prepare a spill management plan by identifying the key chemicals, industries, and areas of concern from historical spill data analysis and stochastic model simulations. This chapter discusses the spill management framework.

6.1. Spill Pollution Prevention Plan

Pollution Prevention (P2) is “the use of processes, practices, materials, products, substances or energy that avoid or minimize the creation of pollutants and waste, and reduce overall risk to human health or the environment” (*Canadian Environmental Protection Act, 1999*). It is at the top of a hierarchy of environmental protection methods that include reuse and recycling, pollution control or treatment, disposal and destruction, and remediation and clean-up due to the most cost-effective opportunities for reducing environmental and health risk. Spill P2 plans (P2P) can eliminate, minimize or reduce the probability of occurrences spill occurrences at source, identify specific spill prevention and management measures to be implemented within the operation over a realistic period of time. The goal of P2P is to protect human health and the environment, specifically protect source water quality in this research.

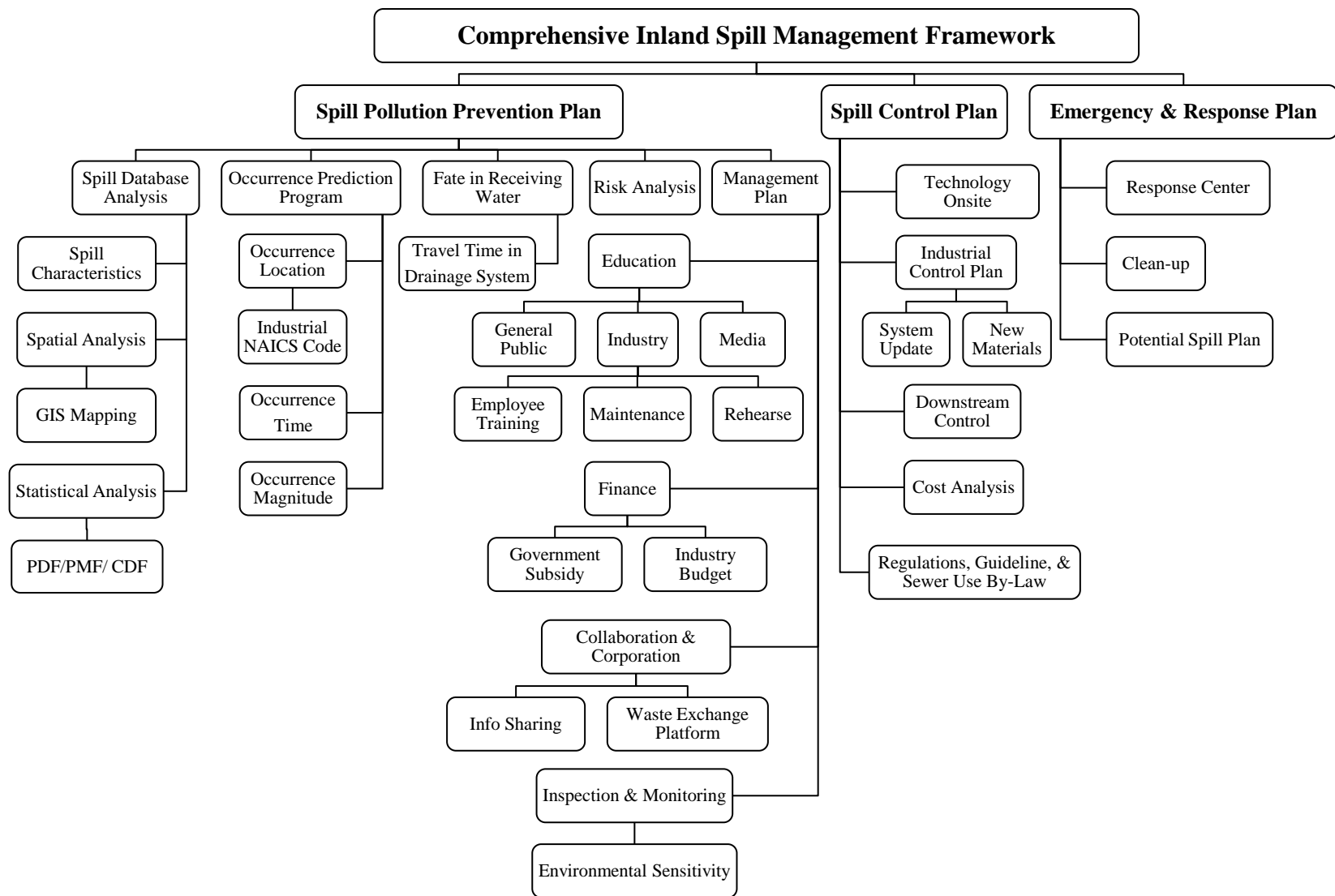


Fig. 6.1: Comprehensive inland spill management framework.

A spill pollution prevention plan (P2P) should consist of spill data analysis, spill occurrence prediction, fate and transport in receiving waters, risk analysis of water quality impairment at downstream locations along the waters, and spill prevention management. Chapter 2 is an example of spill data analysis, which can identify the extent of spill problems and potential locations where prevention management measures should be implemented and resources should be effectively allocated. Chapter 4 provides a spill occurrence prediction simulation model (MMCS model) to simulate quantifiable spill time series (e.g. occurrence number, occurrence times, masses, and locations by mean of NAICS codes). Without models like MMCS, it is difficult to achieve a quantitative risk analysis for water quality impairments at downstream locations along receiving waters. Building upon the MMCS model in Chapter 4, Chapter 5 extends the MMCS model (termed EMMCS model) to analyze associated risks of water quality impairment due to spills at downstream locations along receiving waters. The simulation models, MMCS and EMMCS, provide the planning tools to conduct more research into spill P2P. A prevention management plan can prevent the occurrences of inland spills at source and consists of education programs, finance programs, collaboration and cooperation programs, and inspection and monitoring programs. The previous chapters provided valuable tools for developing such a plan.

6.1.1. Education Programs

An education program is an essential component of a spill P2P. One impetus of this program is to increase public awareness of the occurrences of spill events and encourage them to promptly report the occurrence to regulatory authorities with as much information as they can. Another impetus of this program is to train workers in the relevant industries on preventative maintenance

and operating procedures in order to prevent and reduce spill occurrences. An education program can include employee training, rehearsals, public education, and media response, and can be carried out by governments and industries. The priority industries obtained through MMCS and EMMCS model simulations especially need an education program.

1. Employee training includes preventive maintenance and operation procedures. Maintenance is a key to prevent and reduce spill occurrence on site. Therefore, it is necessary to train employees to be aware of the regular maintenance of equipment and relevant operation procedures. An effective tool is to prepare an operation and maintenance (O&M) schedule. If an O&M schedule exists, it should be reviewed and updated to increase its efficiency and reduce the probability of spill occurrences. This can be achieved by “changing production schedules to minimize equipment and feedstock changeovers, improving maintenance scheduling, segregating by-products at source, training and encouraging staff to improve materials handling and to recognize pollution prevention opportunities, and implementing relatively easily through the introduction of work procedures that target process control systems” (CCME, 2008).
2. Rehearsals are staff training for spill occurrence response and clean-up practices. For instance, emergency response rehearsals could be practiced for evacuating staff from the site, closure of operations, sector, and even the facility if necessary.
3. Public education can be provided through workshops, and seminars. Public education needs to be directed at industries that have spilled in the past or will potentially produce spills in the future (CCME, 2008). A potential spill industry can be identified by model simulations in which the risks of water quality violation at downstream locations are over a specific threshold of probability.

4. Media programs can target audiences through radio, television, newspapers and magazines, internet, flyers, posters, brochures, fact sheets, newsletters, environmental and community groups, and schools and universities (CCME, 2008).

6.1.2. Collaboration and Cooperation Program

Collaboration and cooperation among various facilities or municipalities can enhance spill prevention and reduce spill control costs (e.g. inspection, monitoring, and spill clean-up). Municipalities should also collaborate and cooperate with provincial and federal agencies and industrial associations to promote spill education and training for spill-prone industries (e.g., NAICS 325210). Employee training and preventive maintenance should be emphasized in training programs for spill-prone sectors. For instance, those which have high spill potential should find valuable information through spill data analysis such as spill causes and impacts.

An information sharing platform could be created to provide industries and municipalities information on occurred and potential spill events that are generated through MMCS model, consequences, control measures, clean-up technologies, technologies onsite, etc. Sometimes, information on clean-up technologies specific to industrial sectors can be cost shared and/or specifically developed for the particular spill reduction requirements (CCME, 2008). A waste exchange platform could be helpful for some industries that have opposite chemical properties. For instance, manufacturers of acid and those of bases can exchange their wastes to neutralize their wastewater before discharge. Additionally, information sharing may be needed between countries. For instance, there is a joint committee of Canadian and U.S. municipal people for spill notification.

6.1.3. Inspection and Monitoring Program

An inspection and monitoring program is usually industry-based and should include an inspection and monitoring schedule, maintenance procedures, and a repair and replacement plan if applicable, listing concerned chemicals, probabilistic occurrence time series, physical conditions (e.g., workplace environment and machinery condition), and monitored processes that will potentially produce spill occurrences (e.g., material shipping and storage, manufacturing and operating). An inspection and monitoring schedule should include persons who perform inspection/monitoring, the exact place to be inspected/monitored, the lists of potential or existing hazardous or dangerous materials (e.g. benzene), frequency of inspection and monitoring during a specific period (e.g. quarterly, monthly, etc.), suggested techniques or methods and equipment, and health and safety issues. Maintenance procedures (if non-exist) for the whole industrial processes should be prepared (including pipe systems and equipment) to reduce the possibility of system leakage. Environmental sensitivity is defined as a place, a location, or an area that is sensitive to spills and should be emphasized in an inspection and monitoring program. Important spill information can be derived from analysis of historical data and the risk analysis of spill occurrences using the methods presented in previous chapters.

6.2. Spill Control Plan

A spill control plan involves industry control at source, technology onsite, cost analysis, and relevant downstream control if applicable. Associated regulations, guidelines, acts or by-laws must be emphasized in the spill control plan. All measures used in controlling a spill at source must be cost-effective. If a spill accidentally discharges into receiving waters, downstream water

treatment plants must take action immediately to protect source water quality, human health and ecology health. Downstream governments must announce the situation immediately to the public and report real time treatment progress until the spill is completely controlled.

6.2.1. Technology Onsite

Technology onsite is a highly effective tool for cleaning up and removing spilled chemicals at source. The technology onsite should suit the characteristics of the spilled chemical, be technically and financially feasible, and be applied to control the quality and quantity of a spill onsite prior to release into the environment. A wide variety of characterization, monitoring, and remediation technologies by type, contaminant, or media are listed in the U.S. website for spill clean-up processes (U.S. EPA_a; U.S. EPA_b; U.S. EPA_c), such as:

- Characterization and monitoring technologies by type: fiber optic chemical sensors, gas chromatograph (GC), absorption spectroscopy, infrared spectroscopy and imaging, mass spectrometry, X-ray fluorescence, etc.
- Characterization, monitoring, and remediation technologies by contaminant: arsenic, chromium VI, dense nanaqueous phase liquids (DNAPLs), dioxins, mercury, trichloroethylene (TCE), persistent organic pollutants, and so on.
- Characterization and monitoring technologies by media: gas/air, soil/sediment, and water.
- Remediation technologies by type: bioreactor landfills, in situ chemical reduction, in situ flushing, in situ oxidation, multi-phase extraction, permeable reactive barriers, phytotechnologies, remediation optimization, solvent extraction, soil washing, etc.

Core source control activities in the development of source control best practice have been

discussed by Hew D. McConnell Ltd. (2002), which includes:

1. Routine administration, management, and supervision

- *Program planning and policy development*
- *Program financial management including budgeting, accounting and financial reporting*
- *Staff management, including staff meetings, staff hiring and discipline activities and staff development and training*
- *Public information*
- *Management of award programs*
- *Special studies related to developing and updating program standards and requirements*
- *Internal reports*

2. Source Inspection

- *Site inspections*
- *Facility reviews and updates*
- *Reporting, including preparation of field inspection notes*

3. System Monitoring

- *Technical assessment*
- *Reporting*

4. Enforcement

- *Reviewing monitoring results and development of response actions*
- *Site inspections*
- *Technical assistance*

5. *User Inventory*

- *Identifying, verifying and recording sources, to which source management requirements apply*
- *Recording specifics of authorizations (quantity and quality requirements)*
- *Recording up to date spill characteristics – concentrations and loadings*

6.2.2. Industrial Control Plan

An industrial control plan targets specific sectors that produced spills in the past or have the potential for spills in the future. The two major components are system update and new materials. System update could include equipment modifications and process changes, such as introducing new technologies or approaches to existing operating systems, processes and practices (CCME, 2008). System update provides opportunities to improve the facility's operation.

6.3. Emergency Response Plan

An emergency and response plan could consist of a Response Centre, a Spill Clean-up Plan, and a Potential Spill Plan. Response Centre can be set up in an area that has high frequency of existing or potential spill occurrences or high spilled masses. These information can be obtained through spill database analysis and MMCS model simulations. Under an emergency response plan, a response team could be formed in advance to act promptly when a spill event occurs. Typical response teams are oriented around three entities: Regional Response Team (RRT), Municipal Response Team (MRT), and On-Site Response Team (SRT). Contact information, such as telephone number and person's name, in the case of an emergency should be provided in

an emergency and response plan. Since some municipalities share water resources, such as St Clair River and Lake Ontario with the U.S, emergency response preparedness should consider international cooperation to ensure appropriate and effective preparedness, reporting, and response measures between the two countries when a spill enters the shared water resources.

- RRT is a team consisting of representatives from various municipalities within one or more region. The reason to form a RRT is to recognize the water quality impacts of multiple jurisdictions along the receiving water. The case studies of benzene spills in the St Clair River AOC and the Mimico Creek watershed show that multiple municipalities along the receiving water are affected by the spills. A RRT coordinates planning, preparedness, training and response support on a regional basis and provides support to a MRT.
- MRT is necessary for a municipality that has a high frequency of spill occurrences. A MRT focuses on planning and preparing activities in the event of spill occurrences and obtaining technical and financial support from all possible sources.
- SRT is a response team formed by industries that have a high risk of spill occurrences within a certain time period (e.g. 10 years). The responsibilities of SRT are to prepare emergency response plans for potential spill occurrences, provide activities in the event of spills, and cooperate with and obtain support from MRT and RRT.

6.3.1. Response Centre

A response center will be necessary for emergent spill events within high frequent spill occurrence areas. For a strategic decision making, available components (i.e., equipment, materials, and human resources) must be prepositioned to assure a promptly response to spill events (Wilhelm and Srinivasa, 1997; Srinivasa and Wilhelm, 1997). Spill databases should be

created to record all possible spill information. The written report or a notification after a spill has occurred should include the industrial NAICS code (that is used for spill location PD), the concentration of spill with volume or estimate mass (that is used for spilled mass probability distribution), media into which the spill occurred and associated impacts (i.e. air, surface water, ground water, land, human health, or all of the above), and known or anticipated acute or chronic health risks associated with the spill and advice regarding treatment for exposed individuals and media. Since the current spill database has no information of spill duration time, the model applies a randomly select one within a specific time period. If spill duration time can be recorded or estimated properly, it is very helpful for its probability distribution's determination. The additional information will help to reduce model's epistemic uncertainties.

A map for the recommended positions and industrial locations of spill occurrences can be created by using ArcGIS or other tools and distributed to involved industries and local governments. ArcGIS software can also help to find the shortest distance from response center to occurrence position, so that response teams can reach the spill location at the best time to clean up and control spilled chemicals. For instance, according to the spatial distribution of inland chemical spills in Fig. 3.5, it is clear that these cities should establish spill response centers in order to prepare for spill events and protect source water. By applying ArcGIS tools, the locations of the centers could be considered to be closed to the area with higher spill densities. This arrangement will shorten the travel distance to reach spill locations by the centers' staff.

Industries that have high predictive spill occurrences in the future should have local spill response teams (LSRT) to respond, control, and clean up spills at source immediately. For

instance, according to the MMCS and EMMCS simulations, NAICS 325210 industries in the St Clair River AOC are predicted to have the highest risk of drinking water quality violation at downstream WTP intakes along the River, which is one of the major rivers that has received the most spills and may potentially suffer local water quality impairment. Therefore, the NAICS 325210 industries may need to form a LSRT and prepare associated materials or equipment for controlling and cleaning up benzene spill events. Industrial LSRTs should work closely with the SRCs in various municipalities in addition to government agencies, universities and research centers to prevent and manage inland spills. The spill response centers could subsidize the industrial spill response teams if applicable.

6.3.2. Clean-up Plan

If a spill has occurred and has been transported into a water body, such as a river or a lake, downstream water quality impairments in compliance with associated water quality standards (e.g. maximum acceptable concentration of a chemical in drinking water) must be investigated to ensure a healthy water resource for the ecological environment and human beings. Once the downstream concentrations exceed the limit, actions must be taken and risk-informed decisions must be made to minimize impairments. The first action should be to clean-up at the occurrence site to reduce the continuous discharge of spilled chemicals at source. Therefore, a clean-up plan should be prepared, such as human resources (assigned persons who are responsible for quickly responding to spill events), feasible technologies (e.g., physical/chemical removal or spilled chemical disposal), supported materials and equipment, funding, and so on. Appropriate professional contractors could be available to quickly control emergencies. The technologies onsite as discussed above could be used for cleaning up spilled chemicals.

6.3.3. Spill Potential Plan

If an industry had a high frequency (e.g. twice a year) of predictive spill occurrences or high risk of impaired water quality in the receiving water from MMCS and EMMCS model simulations, a potential spill plan should be included under an ERP so that we can be well prepared for a potential spill event. A PSP should have information on possible industry that can be represented by a NAICS code, location, possible occurrence time, and magnitude. The MMCS model simulation can be used to provide the necessary spill information given enough historical spill data are available. Consequently, it is important to maintain a well-designed and managed spill reporting system.

6.4. Finance Plan

A finance plan in terms of spill management may include government subsidy and industry budget if applicable. Government finance plan should provide information on who needs a subsidy and how much to allocate. An industry finance plan should include the information on why needs governmental finance supports, how to obtain them, and where and how to spend them on spill management. Historical spill analysis and model simulations can provide clues as to which kind(s) of industries should have priority to receive government investment.

An industry is required to provide written proposal that includes all necessary plans discussed in above sections and its own budget to the governments in order to get their supports. After the governments approve and release the subsidy to the industry, the industry is required to report the progress of spill management to the government periodically (e.g., semi-yearly or yearly). If

spill events still occur in the industry, the government can punish it (e.g., penalties) and require a written report to explain its situations and how to improve. It is necessary for the governments to supervise industries on their implementation of spill management, especially those subsidized.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATION

7.1 Conclusions

Inland chemical spills have been identified as one of the major water pollution sources in the Great Lakes basin and have a deleterious effect on the aquatic, terrestrial, and air environment. Every year, hundreds of chemical spills occur in Southern Ontario and likely elsewhere, resulting in surface water pollution and other negative environmental impacts. However, a review of relevant literature revealed that there are few studies on inland spills, except those done at Ryerson University. This study is a comprehensive one, which includes (1) statistical and spatial characteristics analysis for inland chemical spills, (2) model development for simulating probabilistic occurrences of the spills, (3) model development for quantifying associated risks of water quality violations due to spills along receiving rivers, and (4) a comprehensive spill management planning framework.

Based on the study findings, the following conclusions can be drawn:

- The literature review showed that not enough research has been conducted on the effect of chemical spills on fresh inland water and there is a lack of models for predicting the probabilistic quantifiable occurrences of inland spills that can be used to aid decision making.
- River water quality models have been investigated by many researchers. Appropriate models have been chosen for studying the fate of inland spilled chemicals in receiving rivers of Southern Ontario.

- Inland chemical spills in Southern Ontario from 1988-2007 were continuous, complicated, and potential non-point pollutants, which had various impacts on the environment and human health.
- Inland spills are significantly hazardous to receiving water quality according to the analysis of frequency, volumes, and masses, especially as almost half of the spills were not cleaned up.
- The independent spill event characteristics (e.g. inter-event time, mass, etc.) enable stochastic spill models such as MMCS to be developed easily to simulate the probabilistic occurrences of inland spills by time, magnitude, and NAICS-based location. If these event characteristics are inter-dependent, joint distributed spill models must be developed.
- The MMCS model can be easily extended to the EMMCS model for quantifying the risks of water quality impairments due to inland chemical spills. The two models serve to provide technical support for a comprehensive spill management framework.
- The industry's probability of having a specific number of spill occurrences can be determined through the PDF obtained from simulated spill occurrences. With the assistance of spill simulations, the priority of spill prevention and management can be obtained.
- Both MMCS and EMMCS models can be easily re-developed for various characteristics and conditions. For instance, replacing the probabilistic distributions of spill event's variables (i.e. spill inter-event time, spilled mass, and spill NAICS-based location) can switch the models from a large industrial operation (e.g. in the St. Clair River AOC) to a small one (e.g. in Mimico Creek); and applying PDs of river flow rates based on river's characteristics and environmental conditions (no matter how big or small of the river) and appropriate water quality models (e.g. models for big river or small river) can achieve the associated risk

analysis of water quality violation due to the spills.

- Both MMCS and EMMCS models are able to characterize temporal and spatial randomness of any type of chemical/oil spill inland or in water and to quantify aleatory and epistemic uncertainties in face of very limited spill data through integrating the bootstrap resampling technique.
- Two case studies, benzene spills in the St Clair River AOC (real case) and the Mimico Creek watershed (hypothetical case) have been used to demonstrate the MMCS and EMMCS models. The former is conducted for big sizes of industrial operations along a big river with high flow rates, while the latter demonstrates the models for small sizes of industrial operations along a small river with low flow rates.
- As demonstrated by the Mimico case, simulated spill characteristics can be transferred from one area to another area for simulating potential spill probabilistic occurrences and analyzing risks of water quality violation if there are no historical spill records available; in order to have reasonable simulation results to support spill management decision making, industries' operation information (e.g., manufacturing capability, the amount of materials used in the manufacturing processes, and the yield of production) in various areas could be compared to adjust historical spilled mass data. If there is a lack of the information, the spilled mass data can be adjusted through applying the ratio of employee between two industries. The model simulation results could still be used as preliminary clues with respect to the development of a spill prevention and management plan.
- The developed EMMCS model not only can be used by water quality practitioners to predict the probabilistic quantifiable occurrence of inland chemical spills and estimate the associated risks of water quality violations at downstream locations along a river, but also

can be used by regulatory agencies and municipalities to determine the priority industries for spill prevention, control and emergency response, to evaluate the effectiveness of actions against the spills, and to make decisions on where to implement management measures and allocate resources.

- A comprehensive chemical spill management framework, consisting of a spill pollution prevention plan, a spill control plan, and an emergency response plan, can effectively assist a municipality or an industry for inland spill management in order to minimize the spills' potential that threatens human health and/or water quality.

7.2 Recommendation

- The MMCS and EMMCS models require known probability distributions of spill inter-event time, spilled mass, industrial NAICS code, and river flows in order to simulate the probabilistic spill occurrences and quantify risks of water quality violation. Also, the reduction of the model's epistemic uncertainty demands a longer history of sufficient spill data and the information on spill duration time. Therefore, it is recommended to improve spill reporting systems, such as reporting or estimating spill duration time, identifying spill industrial NAICS code and geocoding (i.e. geographic location).
- In the case of benzene spills in the St Clair River Area of Concern, the results indicate two benzene spill occurrences from unknown sources over a 10-year time period, also indicating that spill reporting system needs to be improved to avoid unknown information of a spill (e.g. spill source, location, quantity, etc). Effective staff training and public education should be implemented to reduce unknown information in the spill database.

- Travel time of inland spills in watershed should be estimated if spill sources are located far away from outlets to a waterway. Geographical characteristics of the watershed and municipalities' drainage systems could be involved in the determination of spill travel times from the sources to the outlets to the waterway.
- Further research should consider either field or physical experiments to investigate parameters of water quality model and calibrate the model.
- Spill management planning should be updated periodically using the latest spill database. Additionally, it is recommended that physical or field experiments be conducted to provide data for water quality model calibration.
- This research only focused on dry weather condition. Further research should consider climate and weather conditions for the development of simulation models and spill management framework and the implementation of spill management measures (i.e. inspection, monitoring and training) in accordance with seasonal cycles.

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APPENDIX

A.1 Revised SpillMan Tables

A.1.1 Mean Travel Time (TT) from Outfalls to Intakes

A.1.1.1 TT Applied for River Flow Rate Greater Than 6050 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	6.2	12.0	13.4	20.3	2.9	9.9	4.3	6.2	7.6	11.0	19.7
2	ESSO Chemical	5.4	11.2	12.6	19.5	2.2	9.1	4.2	6.0	7.5	10.9	19.6
3	ESSO (#9 Separator)	5.8	11.6	13.0	19.9	2.5	9.5	4.0	5.9	7.4	10.8	19.4
4	ESSO (#11/12 Separator)	5.2	11.0	12.4	19.3	2.0	8.9	4.0	5.9	7.4	10.8	19.4
5	Polysar (54")	5.6	11.4	12.8	19.7	2.4	9.3	3.9	5.8	7.2	10.6	19.3
6	Polysar (66")	5.5	11.4	12.7	19.7	2.3	9.2	3.8	5.7	7.2	10.6	19.2
7	Polysar (72")	5.5	11.4	12.7	19.7	2.3	9.2	3.8	5.7	7.1	10.6	19.2
8	Sun Oil (Final)	5.0	10.8	12.2	19.1	1.7	8.7	3.4	5.3	6.7	10.1	18.8
9	Talford Ck (Shell Oil)	3.9	9.8	11.1	18.1	0.7	7.6	2.6	4.5	5.9	9.3	18.0
10	Petrosar	3.3	9.1	10.5	17.4	0.1	7.0	2.2	4.1	5.5	8.9	17.6
11	Novacor	2.4	8.2	9.6	16.5	0.0	5.9	1.1	3.0	4.4	7.8	16.5

A.1.1.2 TT Applied for River Flow Rate between 6050 and 4921 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	7.1	13.8	15.4	23.1	3.3	11.3	5.0	7.2	8.9	12.8	23.0
2	ESSO Chemical	6.1	12.9	14.5	22.1	2.5	10.2	4.8	7.0	8.7	12.7	22.8
3	ESSO (#9 Separator)	6.7	13.4	15.1	22.6	2.9	10.9	4.7	6.9	8.6	12.5	22.7
4	ESSO (#11/12 Separator)	5.9	12.6	14.3	21.9	2.3	10.1	4.7	6.9	8.6	12.5	22.7
5	Polysar (54")	6.5	13.2	14.9	22.4	2.7	10.7	4.5	6.7	8.4	12.4	22.5
6	Polysar (66")	6.4	13.1	14.8	22.3	2.6	10.6	4.5	6.7	8.3	12.4	22.5
7	Polysar (72")	6.4	13.1	14.7	22.3	2.6	10.6	4.5	6.7	8.3	12.3	22.5
8	Sun Oil (Final)	5.7	12.4	14.1	21.7	2.0	9.9	3.9	6.2	7.8	11.8	21.9
9	Talford Ck (Shell Oil)	4.5	11.3	12.9	20.5	0.7	8.6	3.0	5.2	6.9	10.9	21.0
10	Petrosar	3.8	10.5	12.2	19.8	0.2	7.9	2.6	4.8	6.4	10.4	20.6
11	Novacor	2.7	9.4	11.1	18.7	0.0	6.7	1.3	3.5	5.1	9.1	19.3

A.1.1.3 TT Applied for River Flow Rate Smaller Than 4921 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	7.6	14.7	16.4	24.5	3.5	12.0	5.4	7.7	9.6	13.7	24.7
2	ESSO Chemical	6.5	13.8	15.5	23.4	2.7	10.8	5.1	7.5	9.3	13.6	24.4
3	ESSO (#9 Separator)	7.2	14.3	16.2	24.0	3.1	11.6	5.1	7.4	9.2	13.4	24.4
4	ESSO (#11/12 Separator)	6.3	13.4	15.3	23.2	2.5	10.7	5.1	7.4	9.2	13.4	24.4
5	Polysar (54")	7.0	14.1	16.0	23.8	2.9	11.4	4.8	7.2	9.0	13.3	24.1
6	Polysar (66")	6.9	14.0	15.9	23.6	2.8	11.3	4.9	7.2	8.9	13.3	24.2
7	Polysar (72")	6.9	14.0	15.7	23.6	2.8	11.3	4.9	7.2	8.9	13.2	24.2
8	Sun Oil (Final)	6.1	13.2	15.1	23.0	2.2	10.5	4.2	6.7	8.4	12.7	23.5
9	Talford Ck (Shell Oil)	4.8	12.1	13.8	21.7	0.7	9.1	3.2	5.6	7.4	11.7	22.5
10	Petrosar	4.1	11.2	13.1	21.0	0.3	8.4	2.8	5.2	6.9	11.2	22.1
11	Novacor	2.9	10.0	11.9	19.8	0.0	7.1	1.4	3.8	5.5	9.8	20.7

A.1.2 Critical Spill Duration Time (TC, in hr) from Outfalls to Intakes

A.1.2.1 TC Applied for River Flow Rate Greater Than 6050 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	0.58	0.83	0.91	0.83	0.41	0.76	4.50	5.50	6.00	7.00	10.00
2	ESSO Chemical	0.49	0.77	0.84	0.77	0.28	0.68	4.40	5.40	5.90	7.00	10.00
3	ESSO (#9 Separator)	0.57	0.83	0.90	0.83	0.39	0.75	4.30	5.30	5.80	6.90	9.90
4	ESSO (#11/12 Separator)	0.49	0.76	0.84	0.76	0.27	0.68	4.30	5.30	5.80	6.90	9.90
5	Polysar (54")	0.57	0.83	0.90	0.83	0.38	0.75	4.20	5.30	5.80	6.90	9.90
6	Polysar (66")	0.56	0.82	0.90	0.82	0.37	0.74	4.20	5.20	5.70	6.80	9.80
7	Polysar (72")	0.56	0.82	0.90	0.82	0.37	0.74	4.20	5.20	5.70	6.80	9.80
8	Sun Oil (Final)	0.53	0.88	0.88	0.80	0.34	0.73	3.90	5.00	5.50	6.70	9.60
9	Talford Ck (Shell Oil)	0.47	0.85	0.85	0.76	0.22	0.68	3.30	0.00	5.10	6.40	9.30
10	Petrosar	0.41	0.72	0.81	0.72	0.09	0.64	0.00	0.00	5.00	6.20	9.10
11	Novacor	0.37	0.70	0.79	0.70	0.00	0.61	0.00	0.00	4.50	5.90	8.70

A.1.2.2 TC Applied for River Flow Rate between 6050 and 4921 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	0.66	0.95	1.04	0.95	0.45	0.84	5.50	6.70	7.30	8.70	11.70
2	ESSO Chemical	0.54	0.87	0.96	0.87	0.32	0.75	5.40	6.60	7.20	8.60	11.60
3	ESSO (#9 Separator)	0.65	0.94	1.03	0.94	0.43	0.83	5.30	6.50	7.20	8.60	11.50
4	ESSO (#11/12 Separator)	0.54	0.86	0.96	0.86	0.31	0.75	5.30	6.50	7.20	8.60	11.50
5	Polysar (54")	0.64	1.03	1.03	0.94	0.42	0.82	5.20	6.50	7.10	8.50	11.40
6	Polysar (66")	0.63	1.03	1.03	0.93	0.41	0.81	5.20	6.40	7.00	8.40	11.40
7	Polysar (72")	0.63	1.03	1.03	0.93	0.40	0.81	5.10	6.40	7.00	8.40	11.40
8	Sun Oil (Final)	0.60	1.01	1.01	0.91	0.35	0.79	4.80	6.10	6.80	8.20	11.20
9	Talford Ck (Shell Oil)	0.53	0.97	0.97	0.87	0.20	0.73	4.10	0.00	6.30	7.80	10.80
10	Petrosar	0.46	0.93	0.93	0.83	0.09	0.69	0.00	0.00	6.10	7.70	10.60
11	Novacor	0.42	0.91	0.91	0.80	0.00	0.66	0.00	0.00	5.50	7.20	10.10

Figure 1A.1.2.3 TC Applied for River Flow Rate Smaller Than 4921 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	0.7	1.0	1.1	1.0	0.5	0.9	6.0	7.3	8.0	9.6	12.6
2	ESSO Chemical	0.6	0.9	1.0	0.9	0.3	0.8	5.9	7.2	7.9	9.4	12.4
3	ESSO (#9 Separator)	0.7	1.0	1.1	1.0	0.5	0.9	5.8	7.1	7.9	9.5	12.3
4	ESSO (#11/12 Separator)	0.6	0.9	1.0	0.9	0.3	0.8	5.8	7.1	7.9	9.5	12.3
5	Polysar (54")	0.7	1.1	1.1	1.0	0.4	0.9	5.7	7.1	7.8	9.3	12.2
6	Polysar (66")	0.7	1.1	1.1	1.0	0.4	0.8	5.7	7.0	7.7	9.2	12.2
7	Polysar (72")	0.7	1.1	1.1	1.0	0.4	0.8	5.6	7.0	7.7	9.2	12.2
8	Sun Oil (Final)	0.6	1.1	1.1	1.0	0.4	0.8	5.3	6.7	7.5	9.0	12.0
9	Talford Ck (Shell Oil)	0.6	1.0	1.0	0.9	0.2	0.8	4.5	0.0	6.9	8.5	11.6
10	Petrosar	0.5	1.0	1.0	0.9	0.1	0.7	0.0	0.0	6.7	8.5	11.4
11	Novacor	0.4	1.0	1.0	0.9	0.0	0.7	0.0	0.0	6.0	7.9	10.8

A.1.3 Time between Arrival and Peak or Peak and Departure (TAPD, in hr) from Outfalls to Intakes

A.1.3.1 TAPD Applied for River Flow Rate Greater Than 6050 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	1.5	2.1	2.3	6.3	1.0	1.9	5.1	6.2	6.7	7.9	11.3
2	ESSO Chemical	1.2	1.9	2.1	6.1	0.7	1.7	5.0	6.1	6.6	7.9	11.2
3	ESSO (#9 Separator)	1.4	2.1	2.3	6.3	0.9	1.9	4.9	6.0	6.6	7.8	11.2
4	ESSO (#11/12 Separator)	1.2	1.9	2.1	6.1	0.7	1.7	4.9	6.0	6.6	7.8	11.2
5	Polysar (54")	1.4	2.1	2.3	6.3	0.9	1.9	4.8	5.9	6.5	7.8	11.1
6	Polysar (66")	1.4	2.1	2.3	6.3	0.9	1.9	4.7	5.9	6.5	7.7	11.1
7	Polysar (72")	1.4	2.1	2.3	6.3	0.9	1.9	4.7	5.9	6.5	7.7	11.1
8	Sun Oil (Final)	1.3	2.0	2.2	6.2	0.9	1.8	4.4	5.6	6.2	7.5	10.8
9	Talford Ck (Shell Oil)	1.2	1.9	2.1	6.1	0.6	1.7	3.7	0.0	5.8	7.2	10.5
10	Petrosar	1.0	1.8	2.0	6.0	0.2	1.6	0.0	0.0	5.6	7.0	10.3
11	Novacor	0.9	0.1	2.0	6.0	0.0	1.5	0.0	0.0	5.1	6.6	9.8

A.1.3.2 TAPD Applied for River Flow Rate between 6050 and 4921 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	1.7	2.4	2.6	7.1	1.1	2.1	6.3	7.6	8.3	9.8	13.2
2	ESSO Chemical	1.4	2.2	2.4	6.9	0.8	1.9	6.1	7.5	8.2	9.7	13.1
3	ESSO (#9 Separator)	1.6	2.4	2.6	7.1	1.0	2.0	6.0	7.4	8.1	9.6	13.0
4	ESSO (#11/12 Separator)	1.4	2.2	2.4	6.9	0.8	1.9	6.0	7.4	8.1	9.6	13.0
5	Polysar (54")	1.6	2.4	2.6	7.1	1.0	2.0	5.9	7.3	8.0	9.5	12.9
6	Polysar (66")	1.6	2.3	2.6	7.0	1.0	2.0	5.8	7.2	7.9	9.5	12.9
7	Polysar (72")	1.6	2.3	2.6	7.0	1.0	2.0	5.8	7.2	7.9	9.5	12.9
8	Sun Oil (Final)	1.5	2.3	2.5	7.0	0.9	2.0	5.4	6.9	7.7	9.3	12.6
9	Talford Ck (Shell Oil)	1.3	2.2	2.4	6.9	0.5	1.8	4.6	0.0	7.1	8.8	12.1
10	Petrosar	1.2	2.1	2.3	6.8	0.2	1.8	0.0	0.0	6.9	8.7	12.0
11	Novacor	1.1	2.0	2.3	6.7	0.0	1.7	0.0	0.0	6.2	8.1	11.4

A.1.3.3 TAPD Applied for River Flow Rate Smaller Than 4921 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	1.8	2.6	2.8	7.5	1.2	2.2	6.9	8.3	9.1	10.8	14.2
2	ESSO Chemical	1.5	2.4	2.6	7.3	0.9	2.0	6.7	8.2	9.0	10.6	14.1
3	ESSO (#9 Separator)	1.7	2.6	2.8	7.5	1.1	2.1	6.6	8.1	8.9	10.5	13.9
4	ESSO (#11/12 Separator)	1.5	2.4	2.6	7.3	0.9	2.0	6.6	8.1	8.9	10.5	13.9
5	Polysar (54")	1.7	2.6	2.8	7.5	1.1	2.1	6.5	8.0	8.8	10.4	13.8
6	Polysar (66")	1.7	2.4	2.8	7.4	1.1	2.1	6.4	7.9	8.6	10.4	13.8
7	Polysar (72")	1.7	2.4	2.8	7.4	1.1	2.1	6.4	7.9	8.6	10.4	13.8
8	Sun Oil (Final)	1.6	2.5	2.7	7.4	0.9	2.1	5.9	7.6	8.5	10.2	13.5
9	Talford Ck (Shell Oil)	1.4	2.4	2.6	7.3	0.4	1.9	5.1	0.0	7.8	9.6	12.9
10	Petrosar	1.3	2.3	2.5	7.2	0.2	1.9	0.0	0.0	7.6	9.6	12.9
11	Novacor	1.2	2.9	2.5	7.1	0.0	1.8	0.0	0.0	6.8	8.9	12.2

A.1.4 General Decay Factors (DF, dimensionless) of Benzene for Various TT

No.	TT (hrs)	DF
1	1-1.9	0.993
2	2-2.9	0.986
3	3-3.9	0.979
4	4-4.9	0.972
5	5-5.9	0.965
6	6-6.9	0.956
7	7-7.9	0.951
8	8-8.9	0.944
9	9-9.9	0.937
10	10-10.9	0.931
11	11-11.9	0.924
12	12-12.9	0.917
13	13-13.9	0.911
14	14-14.9	0.904
15	15-15.9	0.898
16	16-16.9	0.891
17	17-17.9	0.885
18	18-18.9	0.878
19	19-19.9	0.872
20	20-10.9	0.866
21	21-21.9	0.86
22	22-22.9	0.854
23	23-23.9	0.847

A.1.5 No-Decay Peak Concentration for a Loading Rate of 1 kg/s (PC, in ug/L)

A.1.5.1 PC Applied for River Flow Rate Greater Than 6050 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	0.3740	0.1900	0.1700	0.1900	0.1620	0.1510	0.0015	0.0005	0.0009	0.0017	0.0064
2	ESSO Chemical	0.3440	0.1850	0.1670	0.1850	0.1320	0.1490	0.0014	0.0005	0.0009	0.0017	0.0064
3	ESSO (#9 Separator)	0.3950	0.1950	0.1740	0.1950	0.1550	0.1550	0.0013	0.0005	0.0008	0.0016	0.0064
4	ESSO (#11/12 Separator)	0.3510	0.1860	0.1680	0.1860	0.1290	0.1530	0.0013	0.0005	0.0008	0.0016	0.0064
5	Polysar (54")	0.4090	0.1980	0.1770	0.1980	0.1520	0.1580	0.0012	0.0004	0.0008	0.0016	0.0064
6	Polysar (66")	0.4150	0.2000	0.1780	0.2000	0.1480	0.1590	0.0011	0.0004	0.0008	0.0016	0.0065
7	Polysar (72")	0.4160	0.2000	0.1790	0.2000	0.1480	0.1600	0.0011	0.0004	0.0008	0.0016	0.0065
8	Sun Oil (Final)	0.4620	0.2100	0.1870	0.2100	0.1070	0.1680	0.0008	0.0003	0.0006	0.0014	0.0065
9	Talford Ck (Shell Oil)	0.5900	0.2320	0.2050	0.2320	0.0000	0.1900	0.0003	0.0000	0.0004	0.0012	0.0067
10	Petrosar	0.6060	0.2360	0.2070	0.2360	0.0000	0.1970	0.0000	0.0000	0.0003	0.0011	0.0067
11	Novacor	0.7110	0.2530	0.2210	0.2530	0.0000	0.2220	0.0000	0.0000	0.0002	0.0009	0.0068

A.1.5.2 PC Applied for River Flow Rate between 6050 and 4921 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	0.4350	0.2190	0.1970	0.2190	0.1750	0.1800	0.0012	0.0004	0.0007	0.0014	0.0066
2	ESSO Chemical	0.4020	0.2140	0.1920	0.2140	0.1330	0.1780	0.0011	0.0003	0.0006	0.0014	0.0066
3	ESSO (#9 Separator)	0.4600	0.2250	0.2100	0.2250	0.1640	0.1900	0.0010	0.0003	0.0006	0.0014	0.0066
4	ESSO (#11/12 Separator)	0.4130	0.2170	0.1950	0.2170	0.1320	0.1810	0.0010	0.0003	0.0006	0.0013	0.0066
5	Polysar (54")	0.4760	0.2290	0.2040	0.2290	0.1560	0.1950	0.0009	0.0003	0.0006	0.0013	0.0066
6	Polysar (66")	0.4830	0.2310	0.2050	0.2310	0.1470	0.1970	0.0009	0.0003	0.0005	0.0013	0.0066
7	Polysar (72")	0.4850	0.2310	0.2060	0.2310	0.1470	0.1970	0.0009	0.0003	0.0005	0.0013	0.0066
8	Sun Oil (Final)	0.5390	0.2430	0.2150	0.2430	0.0990	0.2080	0.0006	0.0003	0.0004	0.0012	0.0067
9	Talford Ck (Shell Oil)	0.6880	0.2680	0.2360	0.2680	0.0000	0.2360	0.0002	0.0000	0.0003	0.0010	0.0068
10	Petrosar	0.6980	0.2720	0.2380	0.2720	0.0000	0.2400	0.0000	0.0000	0.0002	0.0009	0.0068
11	Novacor	0.8010	0.2720	0.2540	0.2920	0.0000	0.2400	0.0000	0.0000	0.0001	0.0006	0.0068

A.1.5.3 PC Applied for River Flow Rate Smaller Than 4921 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	0.4658	0.2337	0.2106	0.2337	0.1816	0.1947	0.0010	0.0003	0.0005	0.0013	0.0067
2	ESSO Chemical	0.4313	0.2287	0.2046	0.2287	0.1335	0.1927	0.0010	0.0003	0.0005	0.0012	0.0067
3	ESSO (#9 Separator)	0.4928	0.2402	0.2282	0.2402	0.1685	0.2077	0.0009	0.0002	0.0005	0.0012	0.0067
4	ESSO (#11/12 Separator)	0.4443	0.2327	0.2086	0.2327	0.1335	0.1951	0.0009	0.0002	0.0005	0.0012	0.0067
5	Polysar (54")	0.5099	0.2447	0.2176	0.2447	0.1580	0.2137	0.0008	0.0002	0.0005	0.0012	0.0067
6	Polysar (66")	0.5174	0.2467	0.2186	0.2467	0.1465	0.2162	0.0007	0.0002	0.0004	0.0011	0.0067
7	Polysar (72")	0.5199	0.2467	0.2196	0.2467	0.1465	0.2157	0.0007	0.0002	0.0004	0.0011	0.0067
8	Sun Oil (Final)	0.5779	0.2597	0.2291	0.2597	0.0950	0.2282	0.0004	0.0003	0.0003	0.0010	0.0068
9	Talford Ck (Shell Oil)	0.7375	0.2862	0.2517	0.2862	0.0000	0.2592	0.0001	0.0000	0.0002	0.0008	0.0068
10	Petrosar	0.7445	0.2902	0.2537	0.2902	0.0000	0.2617	0.0000	0.0000	0.0001	0.0007	0.0068
11	Novacor	0.8465	0.2816	0.2707	0.3117	0.0000	0.2491	0.0000	0.0000	0.0000	0.0005	0.0068

A.1.6 No-Decay Peak Equilibrium Concentration for a Loading Rate of 1 kg/s (EC, in ug/L)

A.1.6.1 EC Applied for River Flow Rate Greater Than 6050 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	784.0	569.0	558.0	569.0	236.0	413.0	24.8	10.7	19.5	43.4	230.0
2	ESSO Chemical	606.0	509.0	506.0	509.0	135.0	368.0	22.5	9.7	18.1	41.9	229.0
3	ESSO (#9 Separator)	811.0	579.0	568.0	579.0	218.0	420.0	20.7	8.9	17.1	40.7	229.0
4	ESSO (#11/12 Separator)	626.0	16.0	509.0	516.0	127.0	373.0	20.3	8.7	16.9	40.4	229.0
5	Polysar (54")	828.0	585.0	573.0	585.0	211.0	425.0	17.9	8.0	16.1	38.7	228.0
6	Polysar (66")	835.0	588.0	576.0	588.0	201.0	427.0	17.2	7.5	15.5	38.6	228.0
7	Polysar (72")	836.0	588.0	576.0	588.0	201.0	428.0	17.2	7.4	15.4	38.6	228.0
8	Sun Oil (Final)	892.0	606.0	593.0	606.0	130.0	44.0	11.0	5.1	12.1	34.6	226.0
9	Talford Ck (Shell Oil)	1006.0	639.0	625.0	639.0	0.0	466.0	3.2	0.0	7.2	27.7	222.0
10	Petrosar	894.0	617.0	606.0	617.0	0.0	450.0	0.0	0.0	5.5	25.1	220.0
11	Novacor	942.0	641.0	631.0	641.0	0.0	491.0	0.0	0.0	2.2	18.2	214.0

A.1.6.2 EC Applied for River Flow Rate between 6050 and 4921 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	1040.0	751.0	736.0	751.0	284.0	552.0	24.1	9.0	17.6	44.3	275.0
2	ESSO Chemical	786.0	668.0	665.0	668.0	153.0	485.0	21.7	8.1	16.4	42.7	275.0
3	ESSO (#9 Separator)	1070.0	764.0	749.0	764.0	251.0	563.0	19.9	7.4	15.4	41.4	274.0
4	ESSO (#11/12 Separator)	802.0	675.0	671.0	675.0	148.0	490.0	19.5	7.2	15.2	41.1	274.0
5	Polysar (54")	1090.0	772.0	757.0	772.0	231.0	572.0	17.1	6.4	14.4	39.6	273.0
6	Polysar (66")	1100.0	776.0	760.0	776.0	215.0	575.0	15.9	6.1	13.7	38.8	272.0
7	Polysar (72")	1100.0	776.0	761.0	776.0	215.0	575.0	15.9	5.9	13.7	38.8	272.0
8	Sun Oil (Final)	1170.0	799.0	783.0	799.0	124.0	592.0	9.6	3.0	10.3	34.3	270.0
9	Talford Ck (Shell Oil)	1320.0	842.0	823.0	842.0	0.0	622.0	2.4	0.0	5.8	26.9	263.0
10	Petrosar	1170.0	811.0	797.0	811.0	0.0	597.0	0.0	0.0	4.3	24.0	259.0
11	Novacor	1220.0	844.0	832.0	844.0	0.0	650.0	0.0	0.0	1.5	16.5	250.0

A.1.6.3 EC Applied for River Flow Rate Smaller Than 4921 CMS

No.	Intake (upstream to downstream)	1	2	3	4	5	6	7	8	9	10	11
No.	Outfall (upstream to downstream)	Lambton Generating Station	Head of Chenal Ecarte	Walpole Island	Wallaceburg	Stag Island	Fawn Island	St. Clair (Michigan)	East China Twp (Michigan)	Marine City (Michigan)	Algonac (Michigan)	Old Club (Michigan)
1	ESSO (#3 Separator)	1169.4	843.0	825.9	843.0	308.3	622.2	23.7	8.1	16.6	44.8	297.7
2	ESSO Chemical	877.0	748.3	745.3	748.3	162.1	544.1	21.3	7.3	15.5	43.1	298.2
3	ESSO (#9 Separator)	1200.9	857.5	840.5	857.5	267.7	635.3	19.5	6.6	14.5	41.8	296.7
4	ESSO (#11/12 Separator)	890.9	1008.0	752.9	755.3	158.6	549.1	19.1	6.4	14.3	41.5	296.7
5	Polysar (54")	1222.4	866.5	850.0	866.5	241.1	646.3	16.7	5.6	13.5	40.1	295.7
6	Polysar (66")	1233.9	871.0	853.0	871.0	222.1	649.8	15.2	5.4	12.8	38.9	294.2
7	Polysar (72")	1233.4	871.0	854.5	871.0	222.1	649.3	15.2	5.1	12.8	38.9	294.2
8	Sun Oil (Final)	1310.5	896.5	879.0	896.5	121.0	868.9	8.9	1.9	9.4	34.1	292.2
9	Talford Ck (Shell Oil)	1478.7	944.6	923.1	944.6	0.0	700.8	2.0	0.0	5.1	26.5	283.7
10	Petrosar	1309.5	909.0	893.5	909.0	0.0	671.3	0.0	0.0	3.7	23.4	278.7
11	Novacor	1360.5	946.6	933.6	946.6	0.0	730.3	0.0	0.0	1.1	15.6	268.2

A.2 MATLAB Code for Benzene Spills in St. Clair River (Regular Case)

A.2.1 Function Code

```
% return the concentration for all occurrences at each intake

function [array1, array2, count1, count10, count2, count20, CEC, TPK, TPKE, TA, TDe] =
    SpillSim(alpha, beta, mu, sigma, pickorder, IND)
array1 = zeros(7,1);
array2 = zeros(7,1);
Cc = 5;          % critical concentration in river from Drinking Water Act, in ug/L
QQ = 6050;       % average river flow of 6800 (high) and 5300 (low), in m3/s
LQ = 4921;       % average river flow of 4542 (mean monthly minimum) and 5300 (low), in m3/s
count1 = 0;      % count the number of exceedance occurrence at time that is not equal to zero
count10 = 0;     % count the number of exceedance occurrence at time zero
count2 = 0;      % count the number of occurrence at time that is not equal to zero
count20 = 0;     % count the number of occurrence at time zero
DF=0;

mu2 = zeros(1,12);
sigma2 = zeros(1,12);

% loading daily flow rate for each month
load Flow_Jan;
mu_sigma_Jan = lognfit(data_Jan);
mu2(1) = mu_sigma_Jan(1);
sigma2(1) = mu_sigma_Jan(2);

load Flow_Feb;
mu_sigma_Feb = lognfit(data_Feb);
mu2(2) = mu_sigma_Feb(1);
sigma2(2) = mu_sigma_Feb(2);

load Flow_Mar;
mu_sigma_Mar = lognfit(data_Mar);
mu2(3) = mu_sigma_Mar(1);
sigma2(3) = mu_sigma_Mar(2);

load Flow_Apr;
mu_sigma_Apr = lognfit(data_Apr);
mu2(4) = mu_sigma_Apr(1);
sigma2(4) = mu_sigma_Apr(2);

load Flow_May;
mu_sigma_May = lognfit(data_May);
```



```

mu2(5) = mu_sigma_May(1);
sigma2(5) = mu_sigma_May(2);

load Flow_Jun;
mu_sigma_Jun = lognfit(data_Jun);
mu2(6) = mu_sigma_Jun(1);
sigma2(6) = mu_sigma_Jun(2);

load Flow_Jul;
mu_sigma_Jul = lognfit(data_Jul);
mu2(7) = mu_sigma_Jul(1);
sigma2(7) = mu_sigma_Jul(2);

load Flow_Aug;
mu_sigma_Aug = lognfit(data_Aug);
mu2(8) = mu_sigma_Aug(1);
sigma2(8) = mu_sigma_Aug(2);

load Flow_Sep;
mu_sigma_Sep = lognfit(data_Sep);
mu2(9) = mu_sigma_Sep(1);
sigma2(9) = mu_sigma_Sep(2);

load Flow_Oct;
mu_sigma_Oct = lognfit(data_Oct);
mu2(10) = mu_sigma_Oct(1);
sigma2(10) = mu_sigma_Oct(2);

load Flow_Nov;
mu_sigma_Nov = lognfit(data_Nov);
mu2(11) = mu_sigma_Nov(1);
sigma2(11) = mu_sigma_Nov(2);

load Flow_Dec;
mu_sigma_Dec = lognfit(data_Dec);
mu2(12) = mu_sigma_Dec(1);
sigma2(12) = mu_sigma_Dec(2);

% loading SpillMan values
load data_NUMDF
load data_NUMDF_MMQ
load data_EC_MMQ
load data_EC_HQ
load data_EC_LQ
load data_PC_MMQ
load data_PC_HQ

```

```

load data_PC_LQ
load data_TC_MMQ
load data_TC_HQ
load data_TC_LQ
load data_TT_MMQ
load data_TT_HQ
load data_TT_LQ
load data_TAPD_HQ
load data_TAPD_LQ
load data_TAPD_MMQ

t = 0;
To = 365*10;
n = 11;          % 11 intakes along the St. Clair river
CEC = zeros(1,11);
TPK = zeros(1,11);
TPKE = zeros(1,11);
TA = zeros(1,11);
TDe = zeros(1,11);
count = 0;

% Intakes 1 to 11 along the St. Clair River:
% 1 = Lambton Generating Station
% 2 = Head of Chenal Ecarte
% 3 = Walpole Island
% 4 = Wallaceburg
% 5 = Stage Island
% 6 = Fawn Island
% 7 = St. Clair, Michigan
% 8 = East China Twp., Michigan
% 9 = Marin City, Michigan
% 10 = Algonac, Michigan
% 11 = Old Club, Michigan

while 1
    U = rand(1);
    ti = alpha*((log(1/U))^(1/beta)); % inter-event time of spill following Weibull, in day
    t = t + ti; % spill time, in day
    if t > To
        break
    end

    m = lognrnd(mu,sigma); % spilled mass, in kg

    REM = rem(t,365); % the remainder of occurrence time t
    if REM > 1 && REM < 31

```

```

    Q = lognrnd(mu2(1),sigma2(1));
elseif REM > 32 && REM < 59
    Q = lognrnd(mu2(2),sigma2(2));
elseif REM > 60 && REM < 90
    Q = lognrnd(mu2(3),sigma2(3));
    P_Q = logncdf(Q,mu2(3),sigma2(3));
elseif REM > 91 && REM < 120
    Q = lognrnd(mu2(4),sigma2(4));
elseif REM > 121 && REM < 151
    Q = lognrnd(mu2(5),sigma2(5));
elseif REM > 152 && REM < 181
    Q = lognrnd(mu2(6),sigma2(6));
elseif REM > 182 && REM < 212
    Q = lognrnd(mu2(7),sigma2(7));
elseif REM > 213 && REM < 243
    Q = lognrnd(mu2(8),sigma2(8));
elseif REM > 244 && REM < 273
    Q = lognrnd(mu2(9),sigma2(9));
elseif REM > 274 && REM < 304
    Q = lognrnd(mu2(10),sigma2(10));
elseif REM > 305 && REM < 334
    Q = lognrnd(mu2(11),sigma2(11));
else
    Q = lognrnd(mu2(12),sigma2(12));
end

```

```

TD = 3600*((24-0.01)*rand(1) + 0.01);
    % random pick TD between [0.01,24]hr*3600, in second

```

```

Co = 1000*1000*(m/TD)/Q;
    % concentration of spill at river entrance, in ug/L within TD duration time, assuming all
    mass quickly mix with river water, not applicable for the case in St Clair River

```

```

if t ~= 0
    count2 = count2 + 1;
    array2(1, count2) = Co;
    array2(2, count2) = ti;
    array2(3, count2) = t;
    array2(4, count2) = m;
    array2(5, count2) = Q;
    array2(6, count2) = pickorder;
    array2(7, count2) = TD;
else
    count20 = count20 + 1;
end
if Co > Cc

```

```

if t ~= 0
    count1 = count1 + 1;
    array1(1, count1) = Co;
    array1(2, count1) = ti;
    array1(3, count1) = t;
    array1(4, count1) = m;
    array1(5, count1) = Q;
    array1(6, count1) = pickorder;
    array1(7, count1) = TD;
else
    count10 = count10 + 1;
end
end

if Q >= QQ
    for i=1:n
        for j=1:23
            if TT_HQ(IND, i) >= j && TT_HQ(IND, i) < j+1
                DF = data_DF(j);
                break
            end
        end
        if TD/3600 > TC_HQ(IND, i)
            CEC(count + 1, i) = (m*EC_HQ(IND, i)*DF)/TD;
            % the spill conc. at intakes
            TPK(count + 1, i) = TT_HQ(IND, i) + TC_HQ(IND, i)/2;
            % the beginning time of the decay-corrected peak-equilibrium conc. at intakes
            % after the start of a spill, in hr
            TPKE(count + 1, i) = TT_HQ(IND, i) + TD/3600 - TC_HQ(IND, i)/2;
            % the ending time of the decay-corrected peak-equilibrium conc. at the intake
            % after the start of the spill, in hr
            TA(count + 1, i) = TT_HQ(IND, i) - TAPD_HQ(IND, i);
            % the arrival time at the intake of the spill plume, in hr
            TDe(count + 1, i) = TT_HQ(IND, i) + TD/3600 + TAPD_HQ(IND, i);
            % the departure time at the intake of the spill plume, in hr
        else
            CEC(count + 1, i) = (m*PC_HQ(IND, i)*DF);
            TPK(count + 1, i) = TT_HQ(IND, i) + TD/(3600*2);
            % the arrival time at the intake of decay-corrected peak conc., in hr
            TA(count + 1, i) = TT_HQ(IND, i) + TD/(3600*2) - TAPD_HQ(IND, i);
            % the arrival time at the intake of decay-corrected peak conc., in hr
            TDe(count + 1, i) = TT_HQ(IND, i) + TD/(3600*2) + TAPD_HQ(IND, i);
            % the arrival time at the intake of decay-corrected peak conc., in hr
        end
    end
end
elseif Q >= LQ

```

```

for i=1:n
    for j=1:23
        if TT_LQ(IND, i) >= j && TT_LQ(IND, i) < j+1
            DF = data_DF(j);
            break
        end
    end
    if TD/3600 > TC_LQ(IND, i)
        CEC(count + 1, i) = (m*EC_LQ(IND, i)*DF)/TD;
        TPK(count + 1, i) = TT_LQ(IND, i) + TC_LQ(IND, i)/2;
        TPKE(count + 1, i) = TT_LQ(IND, i) + TD/3600 - TC_LQ(IND, i)/2;
        TA(count + 1, i) = TT_LQ(IND, i) - TAPD_LQ(IND, i);
        TDe(count + 1, i) = TT_LQ(IND, i) + TD/3600 + TAPD_LQ(IND, i);
    else
        CEC(count + 1, i) = (m*PC_LQ(IND, i)*DF);
        TPK(count + 1, i) = TT_LQ(IND, i) + TD/(3600*2);
        TA(count + 1, i) = TT_LQ(IND, i) + TD/(3600*2) - TAPD_LQ(IND, i) ;
        TDe(count + 1, i) = TT_LQ(IND, i) + TD/(3600*2) + TAPD_LQ(IND, i);
    end
end
else
    for i=1:n
        for j=1:24
            if TT_MMQ(IND, i) >= j && TT_MMQ(IND, i) < j+1
                DF = DF_MMQ(j);
                break
            end
        end
        if TD/3600 > TC_MMQ(IND, i)
            CEC(count + 1, i) = (m*EC_MMQ(IND, i)*DF)/TD;
            TPK(count + 1, i) = TT_MMQ(IND, i) + TC_MMQ(IND, i)/2;
            TPKE(count + 1, i) = TT_MMQ(IND, i) + TD/3600 - TC_MMQ(IND, i)/2;
            TA(count + 1, i) = TT_MMQ(IND, i) - TAPD_MMQ(IND, i);
            TDe(count + 1, i) = TT_MMQ(IND, i) + TD/3600 + TAPD_MMQ(IND, i);
        else
            CEC(count + 1, i) = (m*PC_MMQ(IND, i)*DF);
            TPK(count + 1, i) = TT_MMQ(IND, i) + TD/(3600*2);
            TA(count + 1, i) = TT_MMQ(IND, i) + TD/(3600*2) - TAPD_MMQ(IND, i) ;
            TDe(count + 1, i) = TT_MMQ(IND, i) + TD/(3600*2) + TAPD_MMQ(IND, i);
        end
    end
end
count = count + 1;
end
end

```

A.2.2 Analysis Code

```
clc; clear

n = 100000; % simulation runs
NAICS = [325210, 100000, 324110, 325110]; % 100000 represents Unknown
P1 = [0.333, 0.308, 0.205, 0.154]; % the frequency of NAICS
TP = 10; % simulation time period
Cc = 5;
tmparray1 = zeros(11,1);
tmparray2 = zeros(11,1);
tmpCEC = zeros(1,11);
tmpTPK = zeros(1,11);
tmpTPKE = zeros(1,11);
tmpTA = zeros(1,11);
tmpTDe = zeros(1,11);
alpha = zeros(1,4);
beta = zeros(1,4);
mu = zeros(1,4);
sigma = zeros(1,4);

load Inter_T_325210
alpha_beta_325210 = wblfit(data_325210_T);
alpha(1) = alpha_beta_325210(1);
beta(1) = alpha_beta_325210(2);
load Mass_325210
mu_sigma_325210 = lognfit(data_325210_M);
mu(1) = mu_sigma_325210(1);
sigma(1) = mu_sigma_325210(2);

load Inter_T_Unknown
alpha_beta_Unknown = wblfit(data_Unknown_T);
alpha(2) = alpha_beta_Unknown(1);
beta(2) = alpha_beta_Unknown(2);
load Mass_Unknown
mu_sigma_Unknown = lognfit(data_Unknown_M);
mu(2) = mu_sigma_Unknown(1);
sigma(2) = mu_sigma_Unknown(2);
load Inter_T_324110
alpha_beta_324110 = wblfit(data_324110_T);
alpha(3) = alpha_beta_324110(1);
beta(3) = alpha_beta_324110(2);
load Mass_324110
mu_sigma_324110 = lognfit(data_324110_M);
mu(3) = mu_sigma_324110(1);
```

```

sigma(3) = mu_sigma_324110(2);
load Inter_T_325110
alpha_beta_325110 = wblfit(data_325110_T);
alpha(4) = alpha_beta_325110(1);
beta(4) = alpha_beta_325110(2);
load Mass_325110
mu_sigma_325110 = lognfit(data_325110_M);
mu(4) = mu_sigma_325110(1);
sigma(4) = mu_sigma_325110(2);

% INDustry outfalls: 325210(4), Unknown(11), 324110(3), 325110(2)
% From upstream to downstream:
% 1 = ESSO(#3 Separator)
% 2 = ESSO Chemical
% 3 = ESSO(#9 Separator)
% 4 = ESSO(#11/12 Separator)
% 5 = Polysar (54")
% 6 = Polysar (66")
% 7 = Polysar (72")
% 8 = Sun,
% 9 = Shell
% 10 = Petrosar
% 11 = Nova Chemical

IND_325210 = [5,6,7,10];
    % index of industry of NAICS 325210 in data TT, TC, EC, PC
IND_100000 = [1,2,3,4,5,6,7,8,9,10,11];
    % index of industry of NAICS Unknown in data TT, TC, EC, PC
IND_324110 = [1,3,4,8,9];
    % index of industry of NAICS 324110 in data TT, TC, EC, PC
IND_325110 = [2,11];
    % index of industry of NAICS 325110 in data TT, TC, EC, PC

for i = 1:4
    param(i).P1 = P1(i);
    param(i).NAICS = NAICS(i);
    param(i).array1 = zeros(11,1);
    param(i).array2 = zeros(11,1);
    param(i).CEC = zeros(1,11);
    param(i).TPK = zeros(1,11);
    param(i).TPKE = zeros(1,11);
    param(i).TA = zeros(1,11);
    param(i).TDe = zeros(1,11);
    param(i).count1 = 0;
    param(i).count10 = 0;
    param(i).count2 = 0;

```

```

    param(i).count20 = 0;
    param(i).count_pick_NAICS = 0;
end

for i = 1:n
    pick_NAICS = rand;
    pick_IND =
        [IND_325210(randint(1,1,[1,length(IND_325210)])),IND_100000(randint(1,1,[1,length(I
            ND_100000)])),IND_324110(randint(1,1,[1,length(IND_324110)])),IND_325110(randint
                (1,1,[1,length(IND_325110)]))];
    if pick_NAICS < 0.333
        param(1).count_pick_NAICS = param(1).count_pick_NAICS + 1;
        pickorder = param(1).array1(6, size(param(1).array1, 2)) + 1;
        IND = pick_IND(1);
        [tmparray1, tmparray2, tmpcount1, tmpcount10, tmpcount2, tmpcount20, tmpCEC, tmpTPK,
        tmpTPKE, tmpTA, tmpTDe] = SpillSim(alpha(1), beta(1), mu(1), sigma(1), pickorder, IND);
        param(1).count2 = param(1).count2 + tmpcount2;
        param(1).count20 = param(1).count20 + tmpcount20;
        param(1).array1 = [param(1).array1, tmparray1];
        param(1).array2 = [param(1).array2, tmparray2];
        param(1).count1 = param(1).count1 + tmpcount1;
        param(1).count10 = param(1).count10 + tmpcount10;
        param(1).CEC = [param(1).CEC; tmpCEC];
        param(1).TPK = [param(1).TPK; tmpTPK];
        param(1).TPKE = [param(1).TPKE; tmpTPKE];
        param(1).TA = [param(1).TA; tmpTA];
        param(1).TDe = [param(1).TDe; tmpTDe];
    elseif pick_NAICS < 0.641
        param(2).count_pick_NAICS = param(2).count_pick_NAICS + 1;
        pickorder = param(1).array1(6, size(param(1).array1, 2)) + 1;
        IND = pick_IND(2);
        [tmparray1, tmparray2, tmpcount1, tmpcount10, tmpcount2, tmpcount20, tmpCEC,
        tmpTPK, tmpTPKE, tmpTA, tmpTDe] = SpillSim(alpha(2), beta(2), mu(2), sigma(2),
        pickorder, IND);
        param(2).count2 = param(2).count2 + tmpcount2;
        param(2).count20 = param(2).count20 + tmpcount20;
        param(2).array1 = [param(2).array1, tmparray1];
        param(2).array2 = [param(2).array2, tmparray2];
        param(2).count1 = param(2).count1 + tmpcount1;
        param(2).count10 = param(2).count10 + tmpcount10;
        param(2).CEC = [param(2).CEC; tmpCEC];
        param(2).TPK = [param(2).TPK; tmpTPK];
        param(2).TPKE = [param(2).TPKE; tmpTPKE];
        param(2).TA = [param(2).TA; tmpTA];
        param(2).TDe = [param(2).TDe; tmpTDe];
    elseif pick_NAICS < 0.846

```



```

    param(3).count_pick_NAICS = param(3).count_pick_NAICS + 1;
    pickorder = param(3).array1(6, size(param(3).array1, 2)) + 1;
    IND = pick_IND(3); % random pick the industry in NAICS 324110
    [tmparray1, tmparray2, tmpcount1, tmpcount10, tmpcount2, tmpcount20, tmpCEC,
    tmpTPK, tmpTPKE, tmpTA, tmpTDe] = SpillSim(alpha(3), beta(3), mu(3), sigma(3),
    pickorder, IND);
    param(3).count2 = param(3).count2 + tmpcount2;
    param(3).count20 = param(3).count20 + tmpcount20;
    param(3).array1 = [param(3).array1, tmparray1];
    param(3).array2 = [param(3).array2, tmparray2];
    param(3).count1 = param(3).count1 + tmpcount1;
    param(3).count10 = param(3).count10 + tmpcount10;
    param(3).CEC = [param(3).CEC; tmpCEC];
    param(3).TPK = [param(3).TPK; tmpTPK];
    param(3).TPKE = [param(3).TPKE; tmpTPKE];
    param(3).TA = [param(3).TA; tmpTA];
    param(3).TDe = [param(3).TDe; tmpTDe];
elseif pick_NAICS < 1
    param(4).count_pick_NAICS = param(4).count_pick_NAICS + 1;
    pickorder = param(4).array1(6, size(param(4).array1, 2)) + 1;
    IND = pick_IND(4);
    [tmparray1, tmparray2, tmpcount1, tmpcount10, tmpcount2, tmpcount20, tmpCEC,
    tmpTPK, tmpTPKE, tmpTA, tmpTDe] = SpillSim(alpha(4), beta(4), mu(4), sigma(4),
    pickorder, IND);
    param(4).count2 = param(4).count2 + tmpcount2;
    param(4).count20 = param(4).count20 + tmpcount20;
    param(4).array1 = [param(4).array1, tmparray1];
    param(4).array2 = [param(4).array2, tmparray2];
    param(4).count1 = param(4).count1 + tmpcount1;
    param(4).count10 = param(4).count10 + tmpcount10;
    param(4).CEC = [param(4).CEC; tmpCEC];
    param(4).TPK = [param(4).TPK; tmpTPK];
    param(4).TPKE = [param(4).TPKE; tmpTPKE];
    param(4).TA = [param(4).TA; tmpTA];
    param(4).TDe = [param(4).TDe; tmpTDe];
end

end

save('param_10yr_1e5.mat','param');

```

A.3 MATLAB Code for Benzene Spills in Mimico Creek

A.3.1 Function Code for Concentration at Mean Stream

% return the conc for the selected location

```
function [array1, array2, count1, count10, count2, count20, Cmax4, tmax4] = SpillSim1(alpha,  
    beta, mu, sigma, pickorder, n4)
```

```
array1 = zeros(6,1);
```

```
array2 = zeros(6,1);
```

```
Cc = 0.005; % critical concentration in river in mg/L
```

```
count1 = 0;
```

```
count10 = 0;
```

```
count2 = 0;
```

```
count20 = 0;
```

```
mu2 = zeros(1,12);
```

```
sigma2 = zeros(1,12);
```

```
load Flow_Jan;
```

```
mu_sigma_Jan = lognfit(Jan_data);
```

```
mu2(1) = mu_sigma_Jan(1);
```

```
sigma2(1) = mu_sigma_Jan(2);
```

```
load Flow_Feb;
```

```
mu_sigma_Feb = lognfit(Feb_data);
```

```
mu2(2) = mu_sigma_Feb(1);
```

```
sigma2(2) = mu_sigma_Feb(2);
```

```
load Flow_Mar;
```

```
mu_sigma_Mar = lognfit(Mar_data);
```

```
mu2(3) = mu_sigma_Mar(1);
```

```
sigma2(3) = mu_sigma_Mar(2);
```

```
load Flow_Apr;
```

```
mu_sigma_Apr = lognfit(Apr_data);
```

```
mu2(4) = mu_sigma_Apr(1);
```

```
sigma2(4) = mu_sigma_Apr(2);
```

```
load Flow_May;
```

```
mu_sigma_May = lognfit(May_data);
```

```
mu2(5) = mu_sigma_May(1);
```

```
sigma2(5) = mu_sigma_May(2);
```

```
load Flow_Jun;
```

```
mu_sigma_Jun = lognfit(Jun_data);
```

```
mu2(6) = mu_sigma_Jun(1);
```

```

sigma2(6) = mu_sigma_Jun(2);

load Flow_Jul;
mu_sigma_Jul = lognfit(Jul_data);
mu2(7) = mu_sigma_Jul(1);
sigma2(7) = mu_sigma_Jul(2);

load Flow_Aug;
mu_sigma_Aug = lognfit(Aug_data);
mu2(8) = mu_sigma_Aug(1);
sigma2(8) = mu_sigma_Aug(2);

load Flow_Sep;
mu_sigma_Sep = lognfit(Sep_data);
mu2(9) = mu_sigma_Sep(1);
sigma2(9) = mu_sigma_Sep(2);

load Flow_Oct;
mu_sigma_Oct = lognfit(Oct_data);
mu2(10) = mu_sigma_Oct(1);
sigma2(10) = mu_sigma_Oct(2);

load Flow_Nov;
mu_sigma_Nov = lognfit(Nov_data);
mu2(11) = mu_sigma_Nov(1);
sigma2(11) = mu_sigma_Nov(2);

load Flow_Dec;
mu_sigma_Dec = lognfit(Dec_data);
mu2(12) = mu_sigma_Dec(1);
sigma2(12) = mu_sigma_Dec(2);

t = 0;
TP = 365*10;
L = 10;
% the length of each compartment of river, in m, applying 0.1, 1, 5, 10, representatively
a = 2.71;    % river width best-fit coefficient (Ref.: Schulze et al.2005)
b = 0.557;   % river width best-fit exponents (Ref.: Schulze et al.2005)
c = 0.349;   % river depth best-fit coefficient (Ref.: Schulze et al.2005)
f = 0.341;   % river depth best-fit exponents (Ref.: Schulze et al.2005)
ke = 0.5;    % benzene evaporation constant, in m/d (Ref.:Schwarzenbach and Gschwend, 1993)
kb = 1.5;    % benzene biodegradation rate, in /day (Ref: Wick et al., 2000)
Cmax4 = zeros(6,1);
tmax4 = zeros(6,1);
count = 0;
while 1

```

```

U = rand(1);
ti = alpha*((log(1/U))^(1/beta));
t = t + ti;    % spill occurrence time, in day
if t > TP
    break
end

```

```

m = lognrnd(mu,sigma);    % spilled mass, in kg

```

```

REM = rem(t,365);
if REM > 1 && REM < 31
    Q = lognrnd(mu2(1),sigma2(1));
elseif REM > 32 && REM < 59
    Q = lognrnd(mu2(2),sigma2(2));
elseif REM > 60 && REM < 90
    Q = lognrnd(mu2(3),sigma2(3));
elseif REM > 91 && REM < 120
    Q = lognrnd(mu2(4),sigma2(4));
elseif REM > 121 && REM < 151
    Q = lognrnd(mu2(5),sigma2(5));
elseif REM > 152 && REM < 181
    Q = lognrnd(mu2(6),sigma2(6));
elseif REM > 182 && REM < 212
    Q = lognrnd(mu2(7),sigma2(7));
elseif REM > 213 && REM < 243
    Q = lognrnd(mu2(8),sigma2(8));
elseif REM > 244 && REM < 273
    Q = lognrnd(mu2(9),sigma2(9));
elseif REM > 274 && REM < 304
    Q = lognrnd(mu2(10),sigma2(10));
elseif REM > 305 && REM < 334
    Q = lognrnd(mu2(11),sigma2(11));
else
    Q = lognrnd(mu2(12),sigma2(12));
end

```

```

TD = 3600*((24-0.01)*rand(1) + 0.01);

```

```

Co = 1000*m/(Q*TD); % concentration of spill at river entrance, in mg/L, assuming all mass
    quickly mix with river water

```

```

W = a*Q^b;
D = c*Q^f;
V = W*D*L;

```

```

if t ~= 0

```

```

    count2 = count2 + 1;
    array2(1, count2) = Co;
    array2(2, count2) = ti;
    array2(3, count2) = t;
    array2(4, count2) = m;
    array2(5, count2) = Q;
    array2(6, count2) = pickorder;
else
    count20 = count20 + 1;
end

if Co > Cc

    count = count + 1;

    if t ~= 0
        count1 = count1 + 1;
        array1(1, count1) = Co;
        array1(2, count1) = ti;
        array1(3, count1) = t;
        array1(4, count1) = m;
        array1(5, count1) = Q;
        array1(6, count1) = pickorder;
    else
        count10 = count10 + 1;
    end

    for i = 1:6
        Cmax4(i, count) = Co/(sqrt(2*pi*(n4(i)-
            1))*(1+V*ke/(Q*D*24*3600)+V*kb/(Q*24*3600))^(n4(i)-1));
        tmax4(i, count) = 24*(n4(i)-1)/(ke/D+kb+24*3600*Q/V);
    end

end

end

end

end

```

A.3.2 Function Code for Concentration at 1/2 and 1/4 Branches

```
function [array1, array2, count1, count10, count2, count20, Cmax2, tmax2, Cmax3, tmax3,
        Cmax4, tmax4] = SpillSim2(alpha, beta, mu, sigma, pickorder, n2, n3, n4)
array1 = zeros(6,1);
array2 = zeros(6,1);
Cc = 0.005;
count1 = 0;
count10 = 0;
count2 = 0;
count20 = 0;

mu2 = zeros(1,12);
sigma2 = zeros(1,12);

load Flow_Jan;
mu_sigma_Jan = lognfit(Jan_data);
mu2(1) = mu_sigma_Jan(1);
sigma2(1) = mu_sigma_Jan(2);

load Flow_Feb;
mu_sigma_Feb = lognfit(Feb_data);
mu2(2) = mu_sigma_Feb(1);
sigma2(2) = mu_sigma_Feb(2);

load Flow_Mar;
mu_sigma_Mar = lognfit(Mar_data);
mu2(3) = mu_sigma_Mar(1);
sigma2(3) = mu_sigma_Mar(2);

load Flow_Apr;
mu_sigma_Apr = lognfit(Apr_data);
mu2(4) = mu_sigma_Apr(1);
sigma2(4) = mu_sigma_Apr(2);

load Flow_May;
mu_sigma_May = lognfit(May_data);
mu2(5) = mu_sigma_May(1);
sigma2(5) = mu_sigma_May(2);

load Flow_Jun;
mu_sigma_Jun = lognfit(Jun_data);
mu2(6) = mu_sigma_Jun(1);
sigma2(6) = mu_sigma_Jun(2);

load Flow_Jul;
```

```

mu_sigma_Jul = lognfit(Jul_data);
mu2(7) = mu_sigma_Jul(1);
sigma2(7) = mu_sigma_Jul(2);

load Flow_Aug;
mu_sigma_Aug = lognfit(Aug_data);
mu2(8) = mu_sigma_Aug(1);
sigma2(8) = mu_sigma_Aug(2);
load Flow_Sep;
mu_sigma_Sep = lognfit(Sep_data);
mu2(9) = mu_sigma_Sep(1);
sigma2(9) = mu_sigma_Sep(2);

load Flow_Oct;
mu_sigma_Oct = lognfit(Oct_data);
mu2(10) = mu_sigma_Oct(1);
sigma2(10) = mu_sigma_Oct(2);

load Flow_Nov;
mu_sigma_Nov = lognfit(Nov_data);
mu2(11) = mu_sigma_Nov(1);
sigma2(11) = mu_sigma_Nov(2);

load Flow_Dec;
mu_sigma_Dec = lognfit(Dec_data);
mu2(12) = mu_sigma_Dec(1);
sigma2(12) = mu_sigma_Dec(2);

t = 0;
TP = 365*10;
L = 10;
% the length of each compartment of river, in m, applying 0.1, 1, 5, 10, representatively
a = 2.71;
b = 0.557;
c = 0.349;
f = 0.341;
ke = 0.5;
kb = 1.5;
Cmax2 = zeros(5,1);
tmax2 = zeros(5,1);
Cmax3 = zeros(5,1);
tmax3 = zeros(5,1);
Cmax4 = zeros(6,1);
tmax4 = zeros(6,1);
count = 0;
while 1

```

```

U = rand(1);
ti = alpha*((log(1/U))^(1/beta));
t = t + ti;
if t > TP
    break
end

m = lognrnd(mu,sigma);

REM = rem(t,365);
if REM > 1 && REM < 31
    Q = lognrnd(mu2(1),sigma2(1));
elseif REM > 32 && REM < 59
    Q = lognrnd(mu2(2),sigma2(2));
elseif REM > 60 && REM < 90
    Q = lognrnd(mu2(3),sigma2(3));
elseif REM > 91 && REM < 120
    Q = lognrnd(mu2(4),sigma2(4));
elseif REM > 121 && REM < 151
    Q = lognrnd(mu2(5),sigma2(5));
elseif REM > 152 && REM < 181
    Q = lognrnd(mu2(6),sigma2(6));
elseif REM > 182 && REM < 212
    Q = lognrnd(mu2(7),sigma2(7));
elseif REM > 213 && REM < 243
    Q = lognrnd(mu2(8),sigma2(8));
elseif REM > 244 && REM < 273
    Q = lognrnd(mu2(9),sigma2(9));
elseif REM > 274 && REM < 304
    Q = lognrnd(mu2(10),sigma2(10));
elseif REM > 305 && REM < 334
    Q = lognrnd(mu2(11),sigma2(11));
else
    Q = lognrnd(mu2(12),sigma2(12));
end

TD = 3600*((24-0.01)*rand(1) + 0.01);

Co = 1000*m/((Q/4)*TD);

W1 = a*(Q/4)^b;
D1 = c*(Q/4)^f;
V1 = W1*D1*L;

if t ~= 0
    count2 = count2 + 1;

```



```

array2(1, count2) = Co;
array2(2, count2) = ti;
array2(3, count2) = t;
array2(4, count2) = m;
array2(5, count2) = Q;
array2(6, count2) = pickorder;
else
    count20 = count20 + 1;
end

if Co > Cc

    W2 = a*(Q/2)^b;
    D2 = c*(Q/2)^f;
    V2 = W2*D2*L;
    W3 = a*Q^b;
    D3 = c*Q^f;
    V3 = W3*D3*L;

    count = count + 1;

    if t ~= 0
        count1 = count1 + 1;
        array1(1, count1) = Co;
        array1(2, count1) = ti;
        array1(3, count1) = t;
        array1(4, count1) = m;
        array1(5, count1) = Q;
        array1(6, count1) = pickorder;
    else
        count10 = count10 + 1;
    end

    for i = 1:5
        Cmax2(i, count) = Co/(sqrt(2*pi*(n2(i)-
            1))*(1+V1*ke/(Q*D1*24*3600/4)+V1*kb/(Q*24*3600/4))^(n2(i)-1)));
        tmax2(i, count) = 24*(n2(i)-1)/(ke/D1+kb+24*3600*Q/(4*V1));
    end

    m1 = Cmax2(5, count)*V1; % in g

    for i = 1:5
        Cmax3(i, count) = (m1/V2)/(sqrt(2*pi*(n3(i)-
            1))*(1+V2*ke/(Q*D2*24*3600/2)+V2*kb/(Q*24*3600/2))^(n3(i)-1)));
        tmax3(i, count) = 24*(n3(i)-1)/(ke/D2+kb+24*3600*Q/(2*V2)); % in hr
    end
end

```

```

m2 = Cmax3(5, count)*V2;

for i = 1:6
    Cmax4(i, count) = (m2/V3)/(sqrt(2*pi*(n4(i)-
        1))*(1+V3*ke/(Q*D3*24*3600)+V3*kb/(Q*24*3600))^(n4(i)-1)));
    tmax4(i, count) = 24*(n4(i)-1)/(ke/D3+kb+Q*24*3600/V3);
end
end

end

end

```

A.3.3 Function Code for Spill Location at 1/2, 1/4 and 1/8 Branches

```

function [array1, array2, count1, count10, count2, count20, Cmax1, tmax1, Cmax2, tmax2,
    Cmax3, tmax3, Cmax4, tmax4] = SpillSim3(alpha, beta, mu, sigma, pickorder, n1, n2, n3, n4)
array1 = zeros(6,1);
array2 = zeros(6,1);
Cc = 0.005;
count1 = 0;
count10 = 0;
count2 = 0;
count20 = 0;

mu2 = zeros(1,12);
sigma2 = zeros(1,12);

load Flow_Jan;
mu_sigma_Jan = lognfit(Jan_data);
mu2(1) = mu_sigma_Jan(1);
sigma2(1) = mu_sigma_Jan(2);

load Flow_Feb;
mu_sigma_Feb = lognfit(Feb_data);
mu2(2) = mu_sigma_Feb(1);
sigma2(2) = mu_sigma_Feb(2);

load Flow_Mar;
mu_sigma_Mar = lognfit(Mar_data);
mu2(3) = mu_sigma_Mar(1);
sigma2(3) = mu_sigma_Mar(2);

load Flow_Apr;

```

```

mu_sigma_Apr = lognfit(Apr_data);
mu2(4) = mu_sigma_Apr(1);
sigma2(4) = mu_sigma_Apr(2);

load Flow_May;
mu_sigma_May = lognfit(May_data);
mu2(5) = mu_sigma_May(1);
sigma2(5) = mu_sigma_May(2);

load Flow_Jun;
mu_sigma_Jun = lognfit(Jun_data);
mu2(6) = mu_sigma_Jun(1);
sigma2(6) = mu_sigma_Jun(2);

load Flow_Jul;
mu_sigma_Jul = lognfit(Jul_data);
mu2(7) = mu_sigma_Jul(1);
sigma2(7) = mu_sigma_Jul(2);

load Flow_Aug;
mu_sigma_Aug = lognfit(Aug_data);
mu2(8) = mu_sigma_Aug(1);
sigma2(8) = mu_sigma_Aug(2);

load Flow_Sep;
mu_sigma_Sep = lognfit(Sep_data);
mu2(9) = mu_sigma_Sep(1);
sigma2(9) = mu_sigma_Sep(2);

load Flow_Oct;
mu_sigma_Oct = lognfit(Oct_data);
mu2(10) = mu_sigma_Oct(1);
sigma2(10) = mu_sigma_Oct(2);

load Flow_Nov;
mu_sigma_Nov = lognfit(Nov_data);
mu2(11) = mu_sigma_Nov(1);
sigma2(11) = mu_sigma_Nov(2);

load Flow_Dec;
mu_sigma_Dec = lognfit(Dec_data);
mu2(12) = mu_sigma_Dec(1);
sigma2(12) = mu_sigma_Dec(2);
t = 0;
TP = 365*10;
L = 10;

```

```

% the length of each compartment of river, in m, applying 0.1, 1, 5, 10, representatively
a = 2.71;
b = 0.557;
c = 0.349;
f = 0.341;
ke = 0.5;
kb = 1.5;
Cmax1 = zeros(5,1);
tmax1 = zeros(5,1);
Cmax2 = zeros(5,1);
tmax2 = zeros(5,1);
Cmax3 = zeros(5,1);
tmax3 = zeros(5,1);
Cmax4 = zeros(6,1);
tmax4 = zeros(6,1);
count = 0;

while 1
    U = rand(1);
    ti = alpha*((log(1/U))^(1/beta));
    t = t + ti;
    if t > TP
        break
    end

    m = lognrnd(mu,sigma);

    REM = rem(t,365);
    if REM > 1 && REM < 31
        Q = lognrnd(mu2(1),sigma2(1));
    elseif REM > 32 && REM < 59
        Q = lognrnd(mu2(2),sigma2(2));
    elseif REM > 60 && REM < 90
        Q = lognrnd(mu2(3),sigma2(3));
    elseif REM > 91 && REM < 120
        Q = lognrnd(mu2(4),sigma2(4));
    elseif REM > 121 && REM < 151
        Q = lognrnd(mu2(5),sigma2(5));
    elseif REM > 152 && REM < 181
        Q = lognrnd(mu2(6),sigma2(6));
    elseif REM > 182 && REM < 212
        Q = lognrnd(mu2(7),sigma2(7));
    elseif REM > 213 && REM < 243
        Q = lognrnd(mu2(8),sigma2(8));
    elseif REM > 244 && REM < 273
        Q = lognrnd(mu2(9),sigma2(9));

```

```

elseif REM > 274 && REM < 304
    Q = lognrnd(mu2(10),sigma2(10));
elseif REM > 305 && REM < 334
    Q = lognrnd(mu2(11),sigma2(11));
else
    Q = lognrnd(mu2(12),sigma2(12));
end

```

```

TD = 3600*((24-0.01)*rand(1) + 0.01);

```

```

Co = 1000*m/((Q/8)*TD);

```

```

W1 = a*(Q/8)^b;
D1 = c*(Q/8)^f;
V1 = W1*D1*L;
if t ~= 0
    count2 = count2 + 1;
    array2(1, count2) = Co;
    array2(2, count2) = ti;
    array2(3, count2) = t;
    array2(4, count2) = m;
    array2(5, count2) = Q;
    array2(6, count2) = pickorder;
else
    count20 = count20 + 1;
end

```

```

if Co > Cc

```

```

    W2 = a*(Q/4)^b;
    D2 = c*(Q/4)^f;
    V2 = W2*D2*L;
    W3 = a*(Q/2)^b;
    D3 = c*(Q/2)^f;
    V3 = W3*D3*L;
    W4 = a*Q^b;
    D4 = c*Q^f;
    V4 = W4*D4*L;

```

```

    count = count + 1;

```

```

    if t ~= 0
        count1 = count1 + 1;
        array1(1, count1) = Co;
        array1(2, count1) = ti;
        array1(3, count1) = t;
    end

```

```

        array1(4, count1) = m;
        array1(5, count1) = Q;
        array1(6, count1) = pickorder;
    else
        count10 = count10 + 1;
    end

    for i = 1:5
        Cmax1(i, count) = Co/(sqrt(2*pi*(n1(i)-
            1))*(1+V1*ke/(Q*D1*24*3600/8)+V1*kb/(Q*24*3600/8))^(n1(i)-1));
        tmax1(i, count) = 24*(n1(i)-1)/(ke/D1+kb+Q*24*3600/(8*V1)); % in s
    end

    m1 = Cmax1(5, count)*V1; % in g

    for i = 1:5
        Cmax2(i, count) = (m1/V2)/(sqrt(2*pi*(n2(i)-
            1))*(1+V2*ke/(Q*D2*24*3600/4)+V2*kb/(Q*24*3600/4))^(n2(i)-1));
        tmax2(i, count) = 24*(n2(i)-1)/(ke/D2+kb+Q*24*3600/(4*V2));
    end

    m2 = Cmax2(5, count)*V2;

    for i = 1:5
        Cmax3(i, count) = (m2/V3)/(sqrt(2*pi*(n3(i)-
            1))*(1+V3*ke/(Q*D3*24*3600/2)+V3*kb/(Q*24*3600/2))^(n3(i)-1));
        tmax3(i, count) = 24*(n3(i)-1)/(ke/D3+kb+Q*24*3600/(2*V3));
    end

    m3 = Cmax3(5, count)*V3;

    for i = 1:6
        Cmax4(i, count) = (m3/V4)/(sqrt(2*pi*(n4(i)-
            1))*(1+V4*ke/(Q*D4*24*3600)+V4*kb/(Q*24*3600))^(n4(i)-1));
        tmax4(i, count) = 24*(n4(i)-1)/(ke/D4+kb+Q*24*3600/V4);
    end
end
end
end
end

```

A.3.4 Analysis Code

```
clc; clear

n = 100000;
TP = 10;
Cc = 0.005; % critical concentration in river from Drinking Water Act, in mg/L
tmparray1 = zeros(6,1);
tmparray2 = zeros(6,1);
tmpCmax1 = zeros(5,1);
tmpCmax2 = zeros(5,1);
tmpCmax3 = zeros(5,1);
tmpCmax4 = zeros(6,1);
tmptmax1 = zeros(5,1);
tmptmax2 = zeros(5,1);
tmptmax3 = zeros(5,1);
tmptmax4 = zeros(6,1);
alpha = zeros(1,3);
beta = zeros(1,3);
mu = zeros(1,3);
sigma = zeros(1,3);

load simulated_inter-event_time_N325210
alpha_beta_325210 = wblfit(simulated_inter-event_time_N325210);
alpha(1) = alpha_beta_325210(1);
beta(1) = alpha_beta_325210(2);
load Sim_mass_325210_adjust
mu_sigma_325210 = lognfit(data_325210_M);
mu(1) = mu_sigma_325210(1);
sigma(1) = mu_sigma_325210(2);

load simulated_inter-event_time_N325110
alpha_beta_325110 = wblfit(simulated_inter-event_time_N325110);
alpha(2) = alpha_beta_325110(1);
beta(2) = alpha_beta_325110(2);
load Sim_Mass_325110_adjust
mu_sigma_325110 = lognfit(data_325110_M);
mu(2) = mu_sigma_325110(1);
sigma(2) = mu_sigma_325110(2);

load simulated_inter-event_time_N324110
alpha_beta_324110 = wblfit(simulated_inter-event_time_N324110);
alpha(3) = alpha_beta_324110(1);
beta(3) = alpha_beta_324110(2);
load Sim_Mass_324110_adjust
mu_sigma_324110 = lognfit(data_324110_M);
```

```
mu(3) = mu_sigma_324110(1);
sigma(3) = mu_sigma_324110(2);
```

```
% Potential INDustries:
% N325210-11 = 1, at 1/4Q branck, in Missisauga
% N325210-12 = 2, at Q main stream, in Missisauga
% N325210-13 = 3, at Q main stream, in Missisauga
% N325110-21 = 4, at 1/8Q branch, in Brampton
% N325110-22 = 5, at Q main stream, in Toronto
% N324110-31 = 6, at 1/8Q branch, in Brampton
% N324110-32 = 7, at 1/4Q branch, in Missisauga
```

```
NAICS = [325210,325110,324110];
IND_325210 = [1,2,3]; % index of industry of NAICS 325210
IND_325110 = [4,5]; % index of industry of NAICS 325110
IND_324110 = [6,7]; % index of industry of NAICS 324110
```

```
count_pick_NAICS_325210 = 0;
count_pick_NAICS_325110 = 0;
count_pick_NAICS_324110 = 0;
for i = 1:7
```

```
    param(i).array1 = zeros(6,1);
    param(i).array2 = zeros(6,1);
    param(i).Cmax1 = zeros(5,1);
    param(i).tmax1 = zeros(5,1);
    param(i).Cmax2 = zeros(5,1);
    param(i).tmax2 = zeros(5,1);
    param(i).Cmax3 = zeros(5,1);
    param(i).tmax3 = zeros(5,1);
    param(i).Cmax4 = zeros(6,1);
    param(i).tmax4 = zeros(6,1);
    param(i).count1 = 0;
    param(i).count10 = 0;
    param(i).count2 = 0;
    param(i).count20 = 0;
    param(i).count_pick_IND = 0;
```

```
end
```

```
% for L = 10 m
n1 = [50, 100, 150, 200, 256; 20, 40, 80, 100, 120];
    % number of apartment for NAICS using 1/8Q
n2 = [20, 30, 40, 50, 64; 50, 100, 150, 200, 254; 40, 80, 100, 120, 164; 10, 16, 20, 24, 30];
    % number of apartment for NAICS using 1/4Q
n3 = [40, 80, 100, 150, 194; 50, 100, 120, 170, 214];
    % number of apartment for NAICS using 1/2Q
```



```
n4 = [448, 848, 1248, 1648, 1948, 2180; 232, 632, 1032, 1432, 1732, 1964; 200, 400, 800, 1200, 1500, 1732];
```

```
% number of apartments for NAICS using Q
```

```
% frequency of NAICSs from the simulation results of the case of St Clair River AOO:  
NAICS 325210 = 0.333, NAICS 325110 = 0.153, and NAICS 324110 = 0.204
```

```
for i = 1:n
```

```
    pick_NAICS = rand;
```

```
    if pick_NAICS < 0.333
```

```
        count_pick_NAICS_325210 = count_pick_NAICS_325210 + 1;
```

```
        pick_IND = IND_325210(randint(1,1,[1,length(IND_325210)]));
```

```
        if pick_IND == 1
```

```
            param(1).count_pick_IND = param(1).count_pick_IND + 1;
```

```
            pickorder = param(1).array1(6, size(param(1).array1, 2)) + 1;
```

```
            [tmparray1, tmparray2, tmpcount1, tmpcount10, tmpcount2, tmpcount20, tmpCmax2,  
             tmptmax2, tmpCmax3, tmptmax3, tmpCmax4, tmptmax4] = SpillSim2(alpha(1),  
             beta(1), mu(1), sigma(1), pickorder, n2(1,:), n3(1,:), n4(1,:));
```

```
            param(1).count2 = param(1).count2 + tmpcount2;
```

```
            param(1).count20 = param(1).count20 + tmpcount20;
```

```
            param(1).array1 = [param(1).array1, tmparray1];
```

```
            param(1).array2 = [param(1).array2, tmparray2];
```

```
            param(1).count1 = param(1).count1 + tmpcount1;
```

```
            param(1).count10 = param(1).count10 + tmpcount10;
```

```
            param(1).Cmax2 = [param(1).Cmax2, tmpCmax2];
```

```
            param(1).Cmax3 = [param(1).Cmax3, tmpCmax3];
```

```
            param(1).Cmax4 = [param(1).Cmax4, tmpCmax4];
```

```
            param(1).tmax2 = [param(1).tmax2, tmptmax2];
```

```
            param(1).tmax3 = [param(1).tmax3, tmptmax3];
```

```
            param(1).tmax4 = [param(1).tmax4, tmptmax4];
```

```
        elseif pick_IND == 2
```

```
            param(2).count_pick_IND = param(2).count_pick_IND + 1;
```

```
            pickorder = param(2).array1(6, size(param(2).array1, 2)) + 1;
```

```
            [tmparray1, tmparray2, tmpcount1, tmpcount10, tmpcount2, tmpcount20, tmpCmax4,  
             tmptmax4] = SpillSim1(alpha(1), beta(1), mu(1), sigma(1), pickorder, n4(2,:));
```

```
            param(2).count2 = param(2).count2 + tmpcount2;
```

```
            param(2).count20 = param(2).count20 + tmpcount20;
```

```
            param(2).array1 = [param(2).array1, tmparray1];
```

```
            param(2).array2 = [param(2).array2, tmparray2];
```

```
            param(2).count1 = param(2).count1 + tmpcount1;
```

```
            param(2).count10 = param(2).count10 + tmpcount10;
```

```
            param(2).Cmax4 = [param(2).Cmax4, tmpCmax4];
```

```
            param(2).tmax4 = [param(2).tmax4, tmptmax4];
```

```
        elseif pick_IND == 3
```

```

param(3).count_pick_IND = param(3).count_pick_IND + 1;
pickorder = param(3).array1(6, size(param(3).array1, 2)) + 1;
[tmparray1, tmparray2, tmpcount1, tmpcount10, tmpcount2, tmpcount20, tmpCmax4,
  tmptmax4] = SpillSim1(alpha(1), beta(1), mu(1), sigma(1), pickorder, n4(2,:));
param(3).count2 = param(3).count2 + tmpcount2;
param(3).count20 = param(3).count20 + tmpcount20;
param(3).array1 = [param(3).array1, tmparray1];
param(3).array2 = [param(3).array2, tmparray2];
param(3).count1 = param(3).count1 + tmpcount1;
param(3).count10 = param(3).count10 + tmpcount10;
param(3).Cmax4 = [param(3).Cmax4, tmpCmax4];
param(3).tmax4 = [param(3).tmax4, tmptmax4];
end

```

```

elseif pick_NAICS < 0.486

```

```

  count_pick_NAICS_325110 = count_pick_NAICS_325110 + 1;
  pick_IND = IND_325110(randint(1,1,[1,length(IND_325110)]));
  if pick_IND == 4
    param(4).count_pick_IND = param(4).count_pick_IND + 1;
    pickorder = param(4).array1(6, size(param(4).array1, 2)) + 1;
    [tmparray1, tmparray2, tmpcount1, tmpcount10, tmpcount2, tmpcount20, tmpCmax1,
      tmptmax1, tmpCmax2, tmptmax2, tmpCmax3, tmptmax3, tmpCmax4, tmptmax4] =
      SpillSim3(alpha(2), beta(2), mu(2), sigma(2), pickorder, n1(1,:), n2(2,:), n3(2,:),
        n4(1,:));
    param(4).count2 = param(4).count2 + tmpcount2;
    param(4).count20 = param(4).count20 + tmpcount20;
    param(4).array1 = [param(4).array1, tmparray1];
    param(4).array2 = [param(4).array2, tmparray2];
    param(4).count1 = param(4).count1 + tmpcount1;
    param(4).count10 = param(4).count10 + tmpcount10;
    param(4).Cmax1 = [param(4).Cmax1, tmpCmax1];
    param(4).Cmax2 = [param(4).Cmax2, tmpCmax2];
    param(4).Cmax3 = [param(4).Cmax3, tmpCmax3];
    param(4).Cmax4 = [param(4).Cmax4, tmpCmax4];
    param(4).tmax1 = [param(4).tmax1, tmptmax1];
    param(4).tmax2 = [param(4).tmax2, tmptmax2];
    param(4).tmax3 = [param(4).tmax3, tmptmax3];
    param(4).tmax4 = [param(4).tmax4, tmptmax4];
  
```

```

elseif pick_IND == 5

```

```

  param(5).count_pick_IND = param(5).count_pick_IND + 1;
  pickorder = param(5).array1(6, size(param(5).array1, 2)) + 1;
  [tmparray1, tmparray2, tmpcount1, tmpcount10, tmpcount2, tmpcount20, tmpCmax4,
    tmptmax4] = SpillSim1(alpha(2), beta(2), mu(2), sigma(2), pickorder, n4(3,:));
  param(5).count2 = param(5).count2 + tmpcount2;
  param(5).count20 = param(5).count20 + tmpcount20;
  param(5).array1 = [param(5).array1, tmparray1];

```

```

param(5).array2 = [param(5).array2, tmparray2];
param(5).count1 = param(5).count1 + tmpcount1;
param(5).count10 = param(5).count10 + tmpcount10;
param(5).Cmax4 = [param(5).Cmax4, tmpCmax4];
param(5).tmax4 = [param(5).tmax4, tmptmax4];
end

```

```

elseif pick_NAICS < 0.69

```

```

count_pick_NAICS_324110 = count_pick_NAICS_324110 + 1;
pick_IND = IND_324110(randint(1,1,[1,length(IND_324110)]));
if pick_IND == 6
    param(6).count_pick_IND = param(6).count_pick_IND + 1;
    pickorder = param(6).array1(6, size(param(6).array1, 2)) + 1;
    [tmparray1, tmparray2, tmpcount1, tmpcount10, tmpcount2, tmpcount20, tmpCmax1,
        tmptmax1, tmpCmax2, tmptmax2, tmpCmax3, tmptmax3, tmpCmax4, tmptmax4] =
        SpillSim3(alpha(3), beta(3), mu(3), sigma(3), pickorder, n1(2,:), n2(3,:), n3(1,:),
            n4(1,:));
    param(6).count2 = param(6).count2 + tmpcount2;
    param(6).count20 = param(6).count20 + tmpcount20;
    param(6).array1 = [param(6).array1, tmparray1];
    param(6).array2 = [param(6).array2, tmparray2];
    param(6).count1 = param(6).count1 + tmpcount1;
    param(6).count10 = param(6).count10 + tmpcount10;
    param(6).Cmax1 = [param(6).Cmax1, tmpCmax1];
    param(6).Cmax2 = [param(6).Cmax2, tmpCmax2];
    param(6).Cmax3 = [param(6).Cmax3, tmpCmax3];
    param(6).Cmax4 = [param(6).Cmax4, tmpCmax4];
    param(6).tmax1 = [param(6).tmax1, tmptmax1];
    param(6).tmax2 = [param(6).tmax2, tmptmax2];
    param(6).tmax3 = [param(6).tmax3, tmptmax3];
    param(6).tmax4 = [param(6).tmax4, tmptmax4];

```

```

elseif pick_IND == 7

```

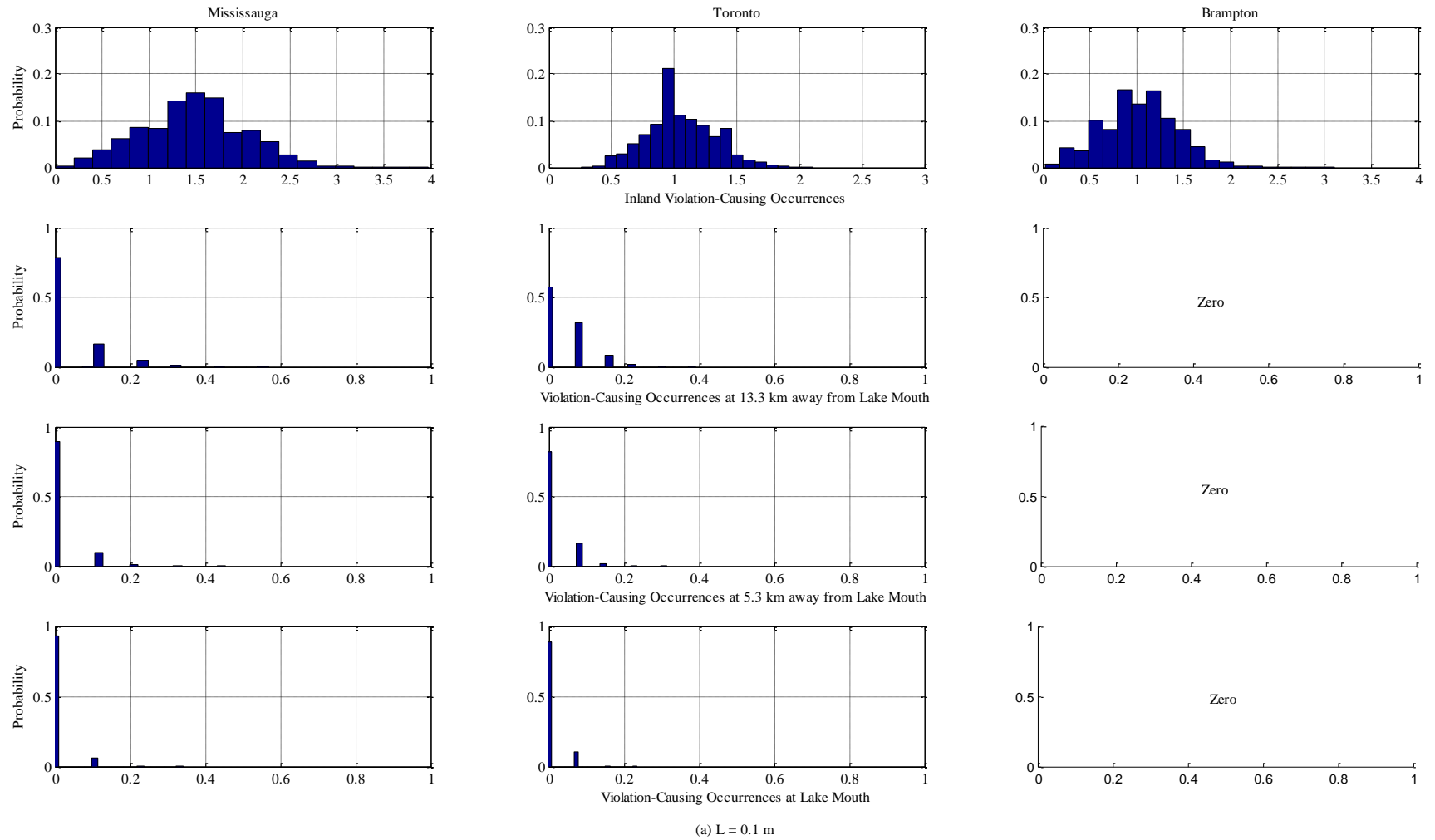
```

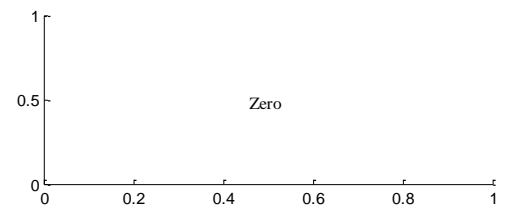
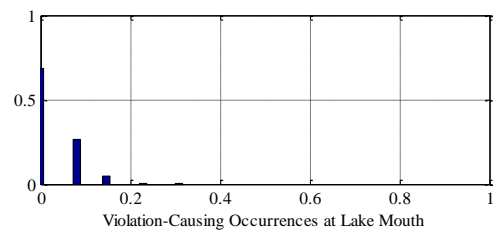
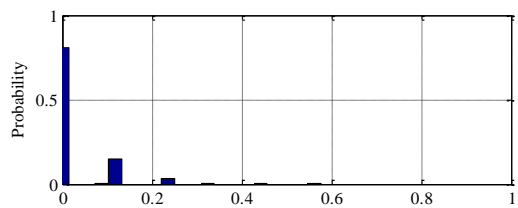
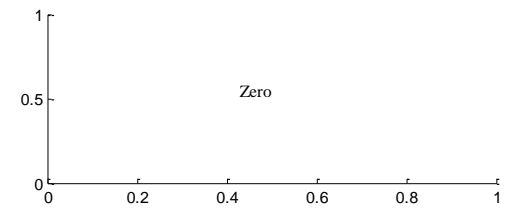
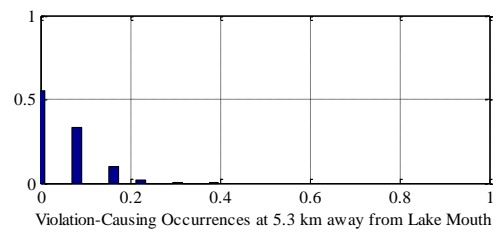
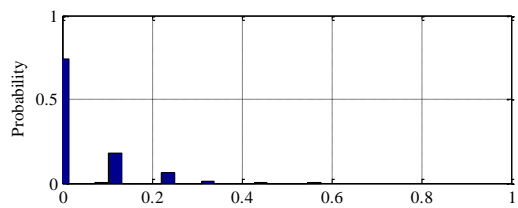
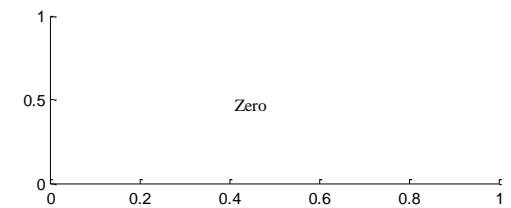
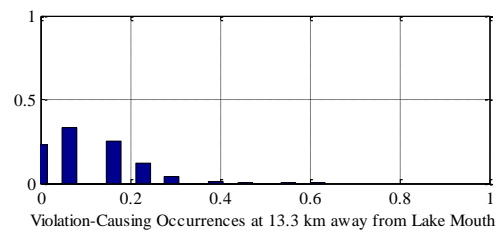
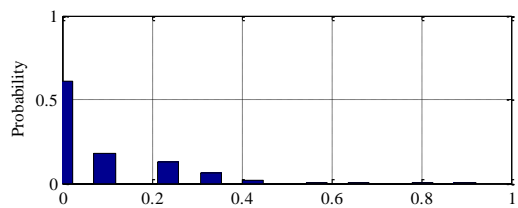
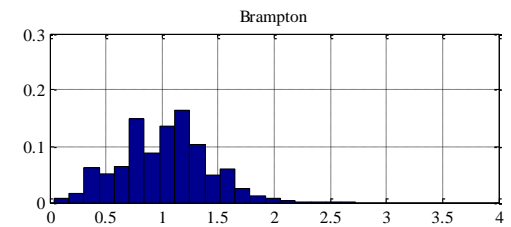
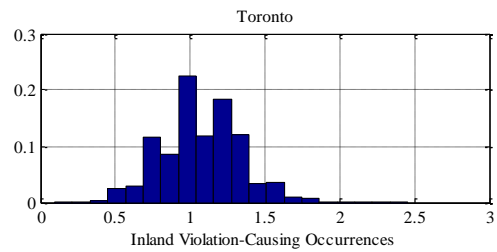
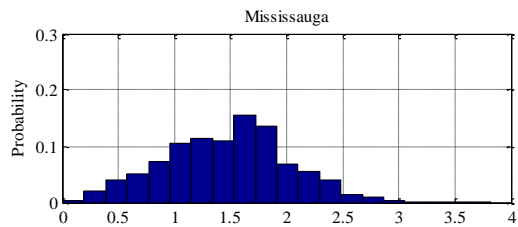
    param(7).count_pick_IND = param(7).count_pick_IND + 1;
    pickorder = param(7).array1(6, size(param(7).array1, 2)) + 1;
    [tmparray1, tmparray2, tmpcount1, tmpcount10, tmpcount2, tmpcount20, tmpCmax2,
        tmptmax2, tmpCmax3, tmptmax3, tmpCmax4, tmptmax4] = SpillSim2(alpha(3),
        beta(3), mu(3), sigma(3), pickorder, n2(4,:), n3(1,:), n4(1,:));
    param(7).count2 = param(7).count2 + tmpcount2;
    param(7).count20 = param(7).count20 + tmpcount20;
    param(7).array1 = [param(7).array1, tmparray1];
    param(7).array2 = [param(7).array2, tmparray2];
    param(7).count1 = param(7).count1 + tmpcount1;
    param(7).count10 = param(7).count10 + tmpcount10;
    param(7).Cmax2 = [param(7).Cmax2, tmpCmax2];
    param(7).Cmax3 = [param(7).Cmax3, tmpCmax3];
    param(7).Cmax4 = [param(7).Cmax4, tmpCmax4];

```

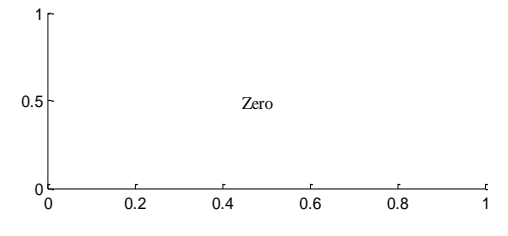
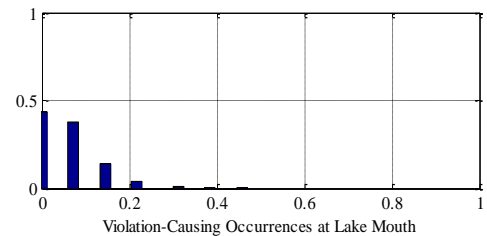
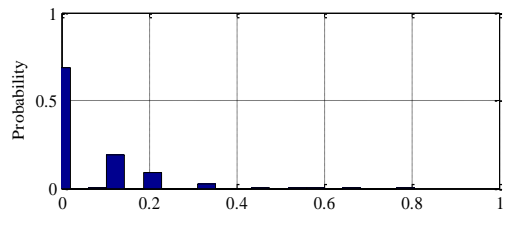
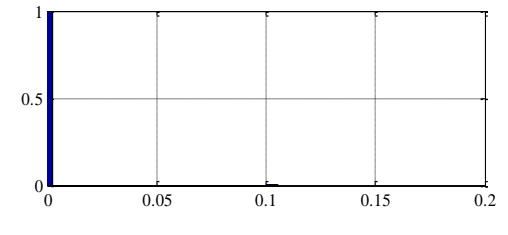
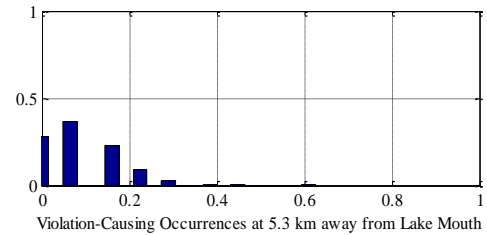
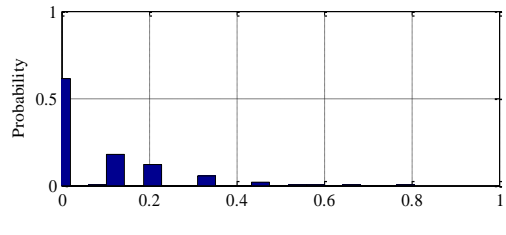
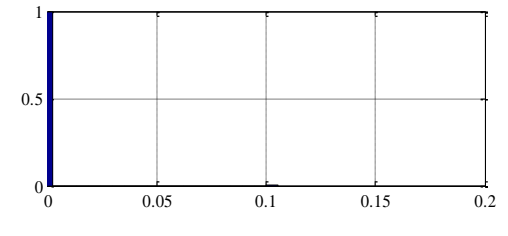
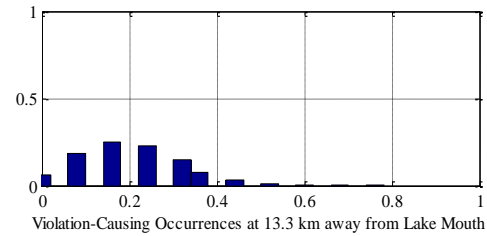
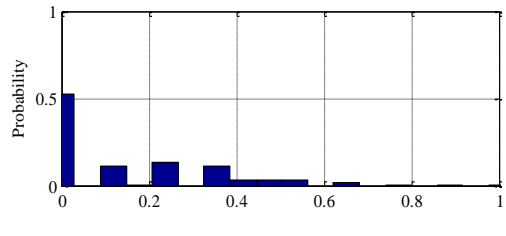
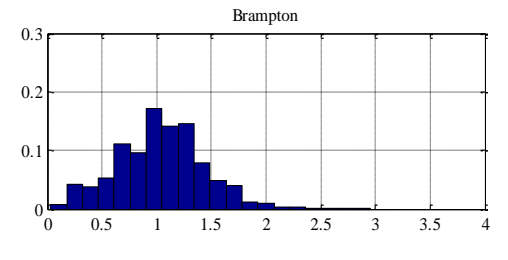
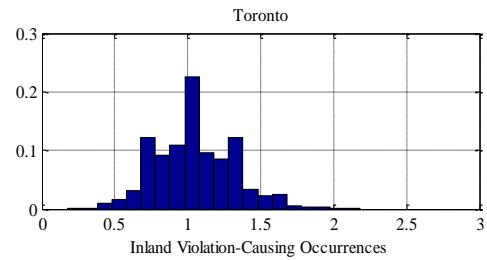
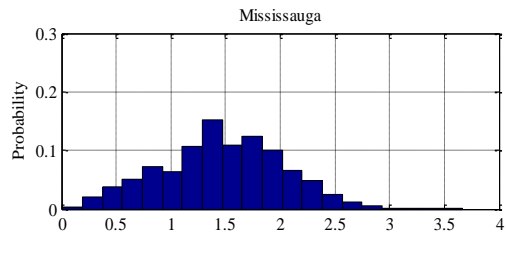
```
        param(7).tmax2 = [param(7).tmax2, tmptmax2];  
        param(7).tmax3 = [param(7).tmax3, tmptmax3];  
        param(7).tmax4 = [param(7).tmax4, tmptmax4];  
    end  
  
end  
  
end  
  
save('param_10yr_1e5_L10.mat','param');
```

A. 4. Histograms of Simulation Results of the Case Study of Mimico Creek Watershed





(b) $L = 1$ m



(c) $L = 5$ m

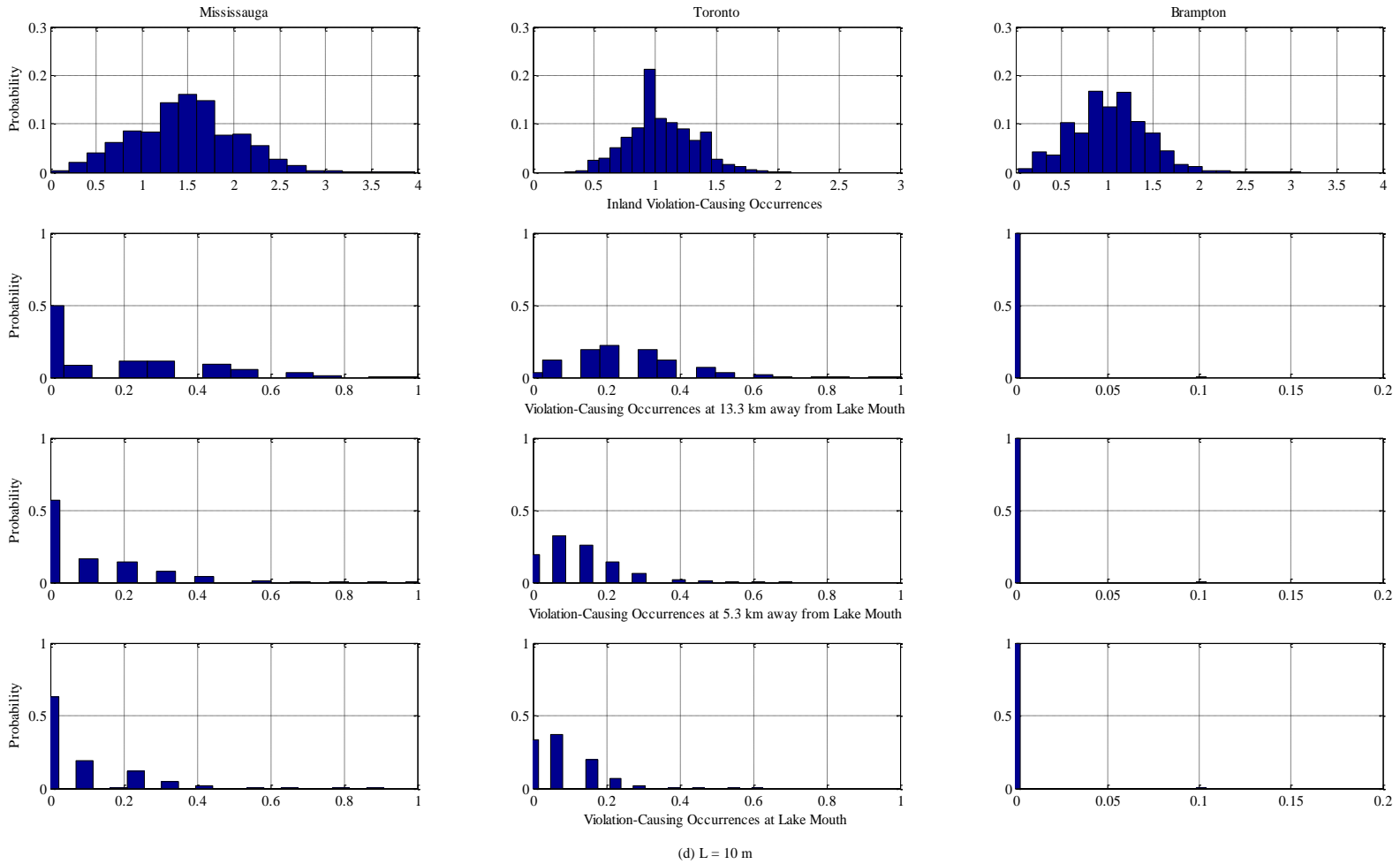
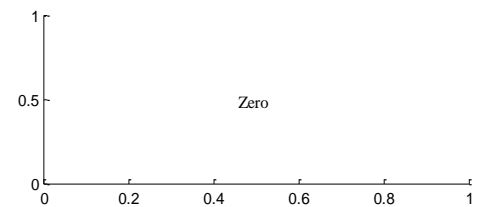
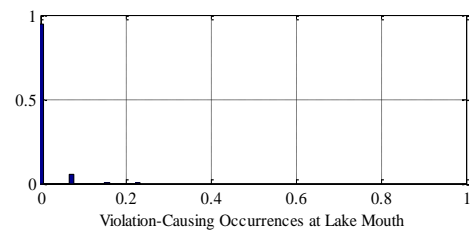
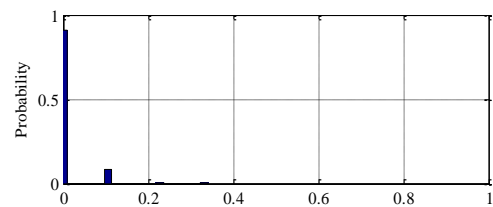
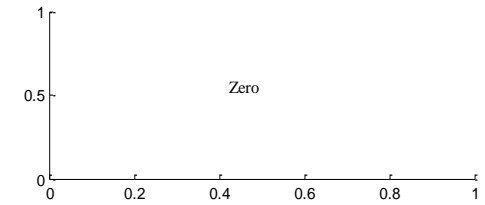
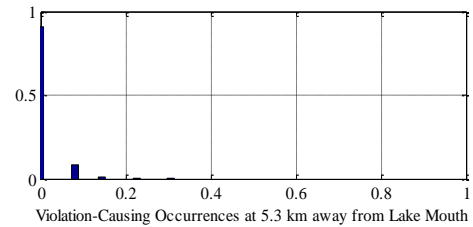
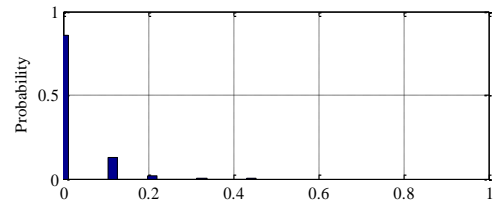
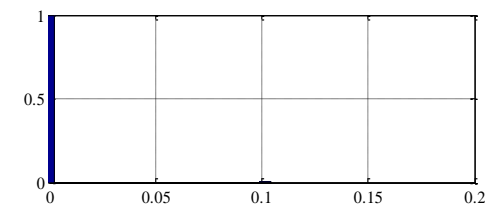
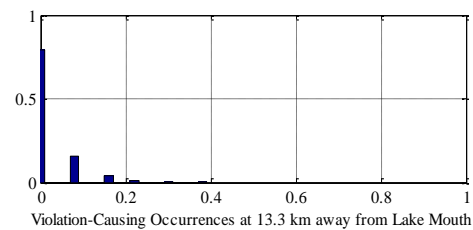
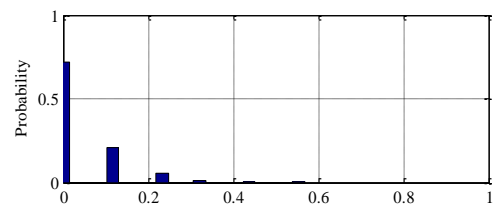
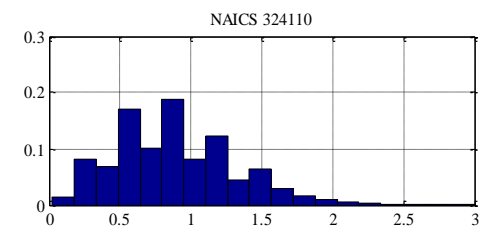
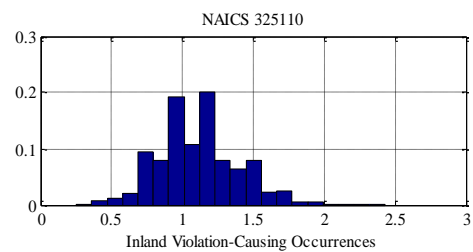
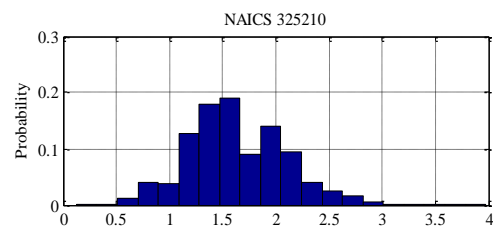
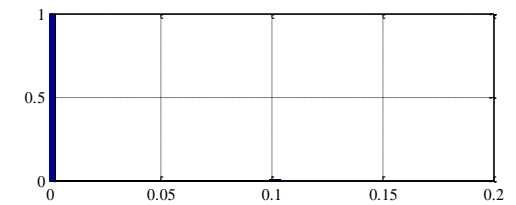
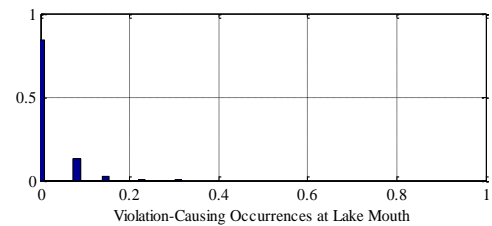
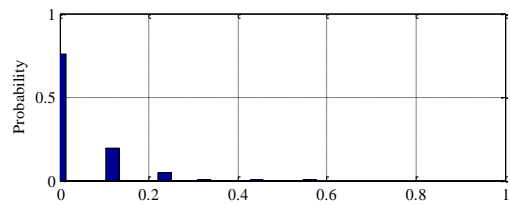
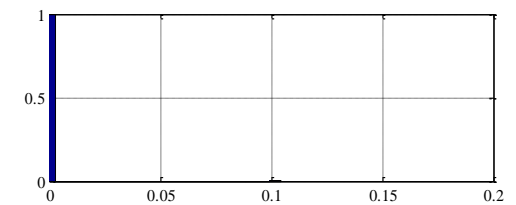
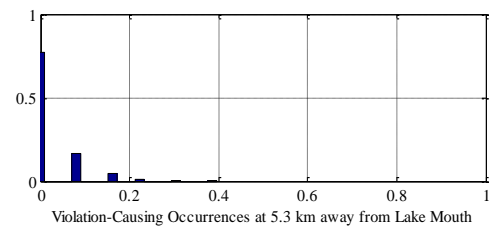
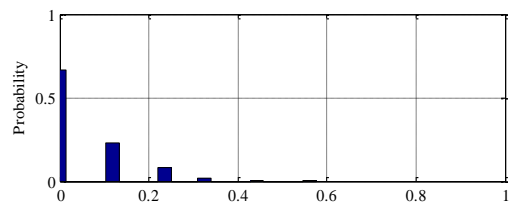
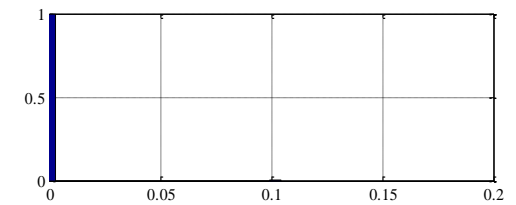
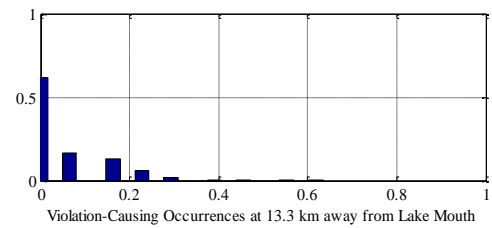
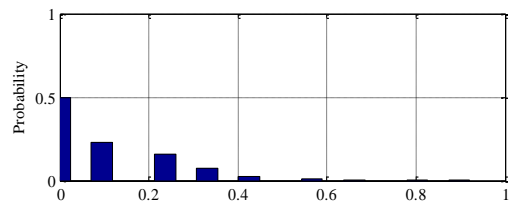
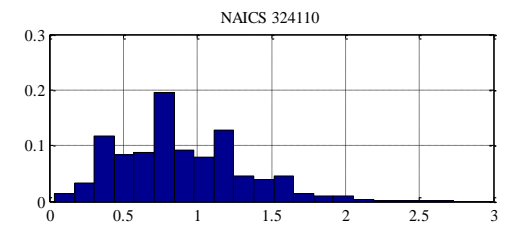
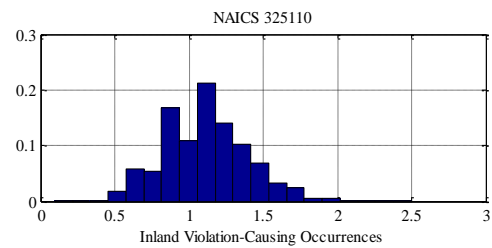
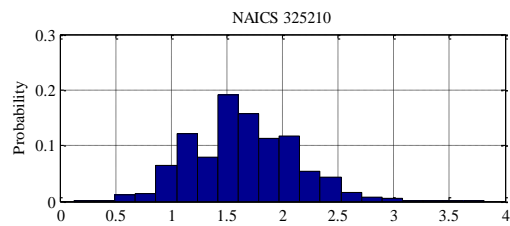


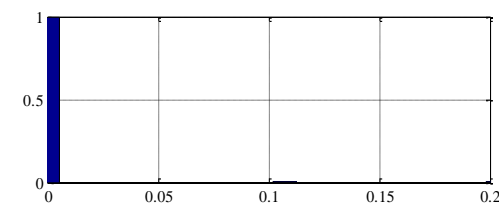
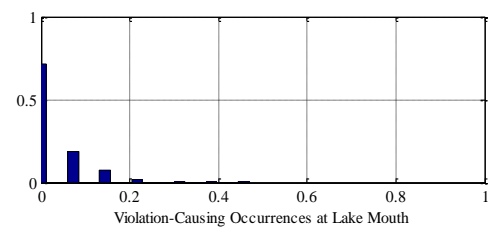
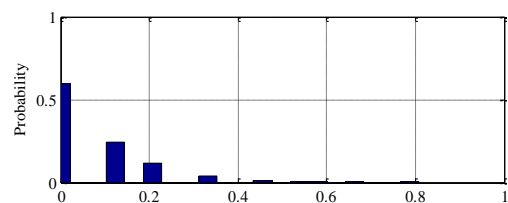
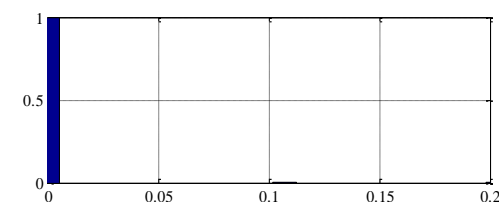
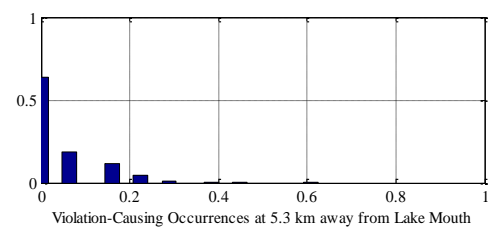
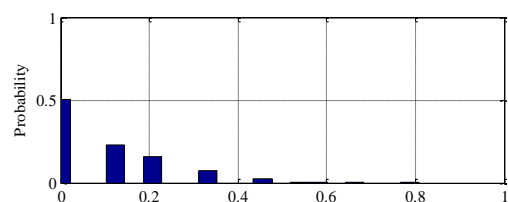
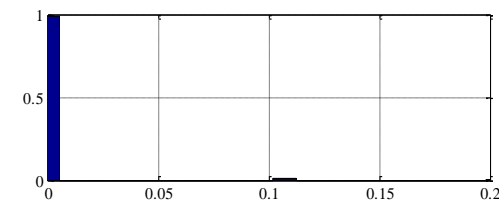
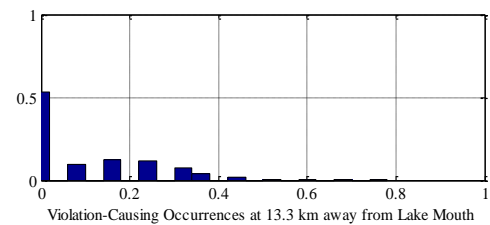
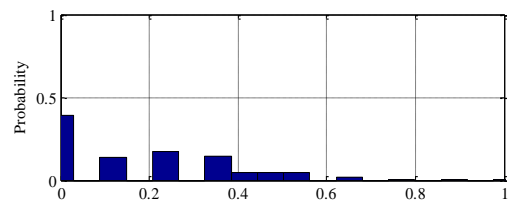
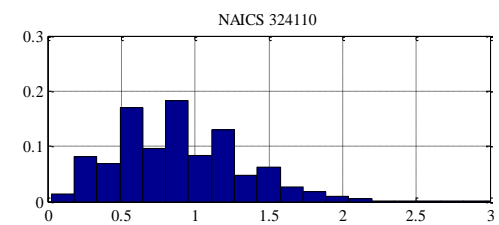
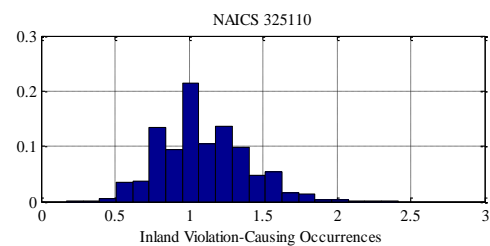
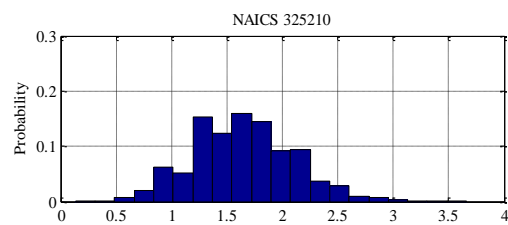
Fig. A.4.1: Histograms of City-based simulated occurrences for a 10-year time period in the Mimico Creek watershed and violation-causing occurrences at selected downstream locations for various scenarios of compartment length: (a) $L = 0.1$ m; (b) $L = 1$ m; (c) $L = 5$ m; (d) $L = 10$ m (10^5 simulation runs and [0.01, 24] hrs of spill duration time).



(a) $L = 0.1$ m



(b) $L = 1$ m



(c) $L = 5$ m

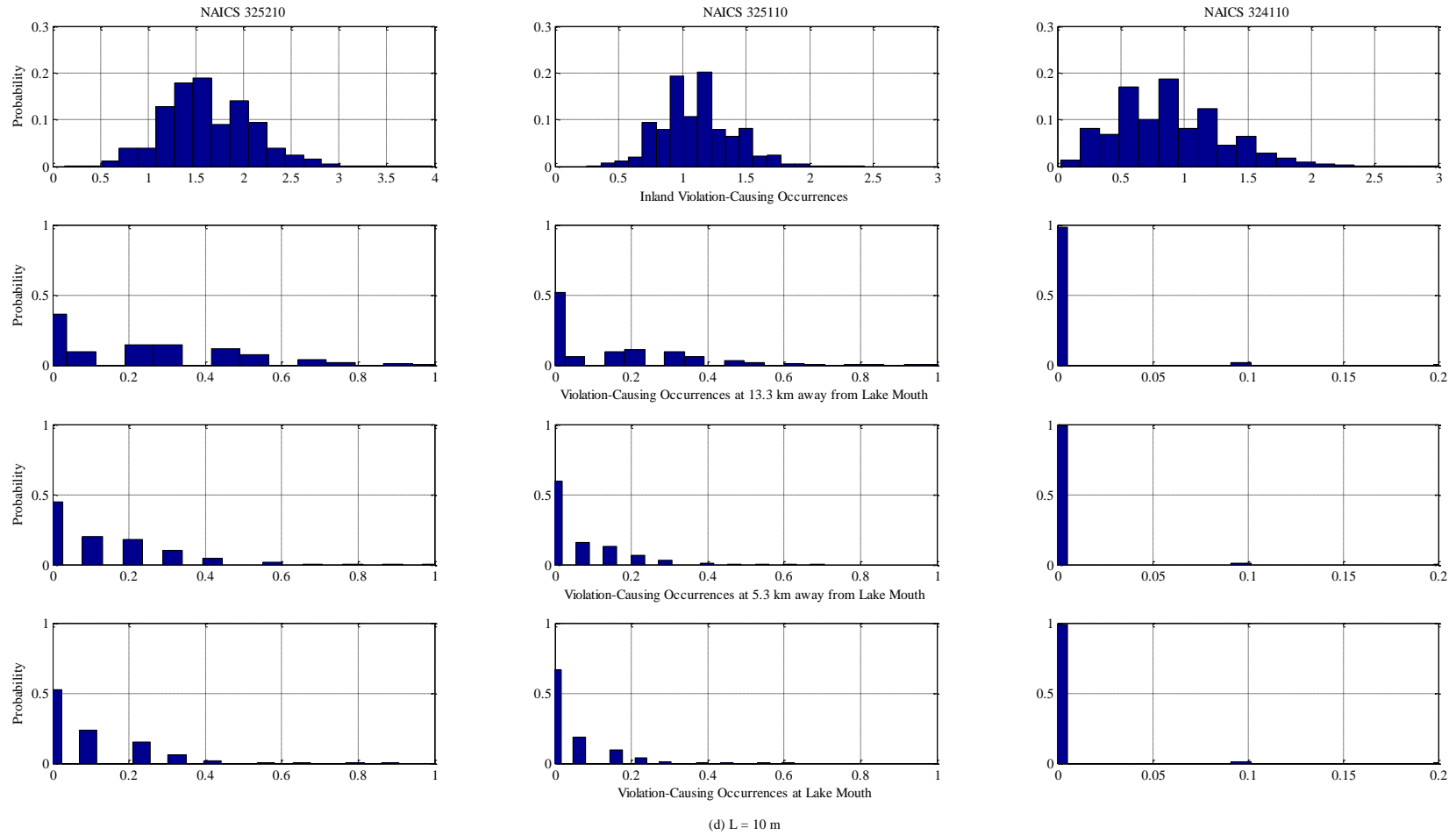


Fig. A.4.2: Histograms of NAICS-based simulated occurrences for a 10-year time period in the Mimico Creek watershed and violation-causing occurrences at selected downstream locations for various scenarios of compartment length: (a) $L = 0.1$ m; (b) $L = 1$ m; (c) $L = 5$ m; (d) $L = 10$ m (10^5 simulation runs and [0.01, 24] hrs of spill duration time).