PROBABILISTIC HUMAN HEALTH RISK ASSESSMENT FROM OFFSHORE PRODUCED WATER

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by

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ABSTRACT

Offshore oil and gas facilities are producing huge amounts of produced water during the production. The produced water contains formation water, injected water, small volumes of condensed water, and any chemical added during production and oil/water separation process. To meet the present regulatory criteria the produced water needs to be treated before discharge to the ocean. But despite the treatment the water contains some contaminants which are chemicals of concern for environment and human health.

Produced water contains both organic and inorganic constituents. Several studies have been conducted in the past to assess their risk associated with produced water. The toxicity and persistence of polycyclic aromatic hydrocarbons (PAHs) in produced water is of particular environmental concern, but there are very few studies on how to asees the associated human health risk. In this study a probabilistic assessment framework was developed to estimate the risk to human health from offshore produced water contaminants, especially PAHs. Two types of fish growth models were compared to select the best model for marine fishes. A questionnaire survey was conducted to get information about the local trend of fish ingestion and other demographic information. The concentrations of PAHs were considered absorbed in the lipids of fish and along with the food chain ingested into the human body. The probabilistic results were compared with the deterministic analysis. The hazard values were to be negligible, but the risk values were found to be slightly above the U.S. Environmental Protection Agency (USEPA) acceptable limit. The probable main reasons for this were lack of data regarding concentrations of contaminants in produced water and values of slope factor of PAHs. The probabilistic framework is flexible and can be extended for use to other contaminants of produced water. A set of recommendations were included for future studies.

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I would like to dedicate this work to our new born daughter Sarah Hassan.

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a	Growth parameter for particular fish
b	Slope of the growth-length curve
C_o	Concentration of pollutant at the discharge point
C_1, C_2, C_3, C_4	Length-Age coefficients
C_{exp}	Exposure concentration for fish
C_f	Concentration in fish tissue
C_L	Concentration of contaminant in lipid of a fish
HQ_i	Hazard quotient for contaminant i
D	Water depth
F_{epr}	Ratio between the weight of edible part to the weight of whole fish
F_L	Fraction lipid concentration in fish
Fr	Fraction of ingested fish
I	Total pollutant intake, chronic daily intake
k	Relative growth rate parameter/The rate of exponential decrease of the relative growth rate with age/Curvature parameter
K_Z	Vertical diffusion coefficient
$L\infty$	Asymptotic length at infinitely long period
L_t	Length of fish at age t
L_{max}	Maximum length
Q_e	Effluent flow
Q	Effluent discharge rate
R	Risk or hazard value for a particular pollutant
R_i	Cancer risk from pollutants i
t	Age in yr
t_0	The age when an individual fish would have been of zero

	length assuming the equation to be valid at all ages/Condition parameter
u	Ambient current velocity
V	Ambient flow velocity
v	Horizontal diffusion velocity
W	Weight of the fish at particular age
w	Width of zone of dilution
W_c	Total accumulated contaminants in fish
W_t	Weight of fish
x	Horizontal length of consideration
λ	Theoretical initial relative growth rate at zero age

List of Abbreviations

AT	Averaging Time
AUV	Autonomous Underwater Vehicle
BAF	Bio-available factor
BAT	Best available technology
bbls	Barrels
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
BTX	Benzene, Toluene and Xylenes
BCF	Bio-concentration factor
BW	Body Weight
CCME	Council of Ministers of the Environment
C-NLOPB	Canada-Newfoundland Offshore Petroleum Board
COOGER	The Centre for Offshore Oil, Gas and Energy Research
CORMIX	The Cornell Mixing Zone Expert System
DFO	Fisheries and Oceans Canada
DREAM	The Dose Response Effects Assessment Model
DISSPROWM	Decision Support System for Produced Water Management
CHARM	Chemical Hazard Assessment and Risk Management
EC	Exposure Concentration
EC_{50}	Concentration that restricts growth of 50% of the exposed population
ED	Exposure Duration
EF	Exposure Frequency
ERA	Ecological Risk Assessment
FIR	Fish Ingestion Rate
FPSO	Floating Production, Storage and Offloading
GBS	Gravity Base Structure
GUI	Graphical User Interface
HI	Total hazard for a specific pathway

HQ	Hazard quotient
LC_{50}	Concentration that kills 50% of the exposed population
Mbbls	Thousand barrels
MMS	Minerals Management Service
NPD	Napthalene, Phenanthrene and Dibenzothiophene
NORM	Naturally Occurring Radioactive Materials
NRC-NAS	The National Research Council of the National Academy of Sciences
NSCRF	The National Study of Chemical Residues in Fish
OSPAR	The Oslo Paris Commission
PAHs	Polycyclic Aromatic Hydrocarbons
pCi	Picocuries, unit of radioactivity
ppt	parts per trillion
RAIS	Risk Assessment Information System
R_fD	Reference dose of the pollutant chemicals
RPFs	relative potency factors
ROPME	Regional Organization for Protection of the Marine Environment
GBS	Gravity Based Structure
SF	Cancer slope factor
STORET	The Storage and Retrieval database
TEFs	Toxic equivalency factors
USEPA	US Environmental Protection Agency
VBG	Von Bertalanffy Growth
VGBM	Von Bertalanffy Growth Model
WERF	Water Environment Research Foundation

Chapter 1

INTRODUCTION

1.1 Background

Environmental pollution is one of the major issues in the marine ecosystem and in recent years this problem is increasing due to increasing offshore and onshore activities. Offshore oil and gas production related pollutants are the greatest among all pollutants released to the ocean (Khan and Islam, 2005) due to vast offshore activities. During the offshore oil and gas production vast amounts of formation water are brought up from the reservoirs.

Veil et al. (2005) defined produced water as the water trapped in underground formations that is brought to the surface along with oil or gas. It is the largest wastewater stream associated with oil and gas production. It consists of formation water (water naturally present in the reservoir), flood water (water previously injected into the formation to maintain reservoir pressure), and condensed water (in the case of gas production) as well as chemicals added during production process (CAPP, 2001). The formation water lays under the hydrocarbon layers and is the main source of chemicals in the produced water.

The constituents of produced water contain a number of contaminants of environmental concern including hydrocarbons, nutrients, brine, injected water to the well, any chemical additives, heavy metals, Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX), phenols, Polycyclic Aromatic Hydrocarbons (PAHs), naturally occurring radioactive materials (NORM) etc (DFO, 2009). The oil and water is usually separated on the platform. After separation, the oil and gas are sent to shore by pipeline or transported to shore by tanker, and the produced water is either discharged to the sea or reinjected into the reservoir after different treatment to meet with the regulatory standards.

The discharge of produced water from Norwegian oil and gas production was 144 million m^3 in 2006 while the total global production was 173 million m^3 (OLF, 2006). In the Gulf of Mexico in the USA, the typical daily discharge varies from 3000 to 32000 m^3/day (Veil et al., 2005). In the Java Sea, the discharge rate is 123,000 m^3/day (Mukhtasor, 2001). Produced water amount can vary from 2-98% of the extracted fluids from the oil and gas wells (Wiedman, 1996).

The amount of produced water generation is site specific and it increases as the oil fields become matured. In 2003 USEPA estimated the ratio of oil and water in the produced water was from 0.1 to 12.6%. Plebon et al. (2007) reported that globally three barrels of water are produced for every barrel of crude oil and for North America the ratio is approaching 10:1. Also Vik (2007) mentioned that the production of water from the oil industry is more than three times larger than the oil production. As a result of this increasing produced water production the water cut is 75% and is steadily increasing.

Produced water, before being discharged to the sea, needs to be treated to meet the regulatory standards. The choice of treatment, however, depends on many factors and studies are being conducted for better treatment technologies to meet the tougher regulatory demands. But despite the treatment, there is concern that produced water contaminants may create environmental effects on fish, microbial ecology and food habitats (DFO, 2009). The Centre for Offshore Oil, Gas, and Energy Research (COOGER, 2009) reported exposure of fertilized eggs to produced water could affect early cell division in fish embryos of COD in the Atlantic Ocean.

The individual constituents of produced water can have potential toxic effects and chemical reactions with seawater can produce solids that can change the nature of sediments both chemically and physically (Orszulik, 2007). The Oslo Paris Commission (OSPAR, 2007) reported modification of benthic fauna and 155 km^2 of contaminated area in the Norwegian continental shelf. Metal specific toxicological studies show that LC_{50} of Arsenic for seawater crustaceans for an exposure period of 8 to 51 days varies from 893 to 7,000 μg/l (ANWQG, 2000). Several studies to assess the risk from produced water constituents for marine fishes have been reported (Øfjord et al., 1996). Ecological risk assessments from produced water were conducted by Neff et. al. (2006), Chowdhury et. al. (2004), Karman et al. (1996), Stephens et al. (1996) and Furuholt (1996).

Produced water, once discharged, goes through quick dilution; and the rate of dilution is very high within 50-100 m from the discharge point (Mukhtasor, 2001). To calculate the dilution there are a number of models available. Among them The Dose Response Effects Assessment Model (DREAM), The Cornell Mixing Zone Expert System (CORMIX), Chemical Hazard Assessment and Risk Management (CHARM) are prominent. The DREAM model was developed by Johnson (1999) and incorporates the complex biological exposure in the dilution model. Therefore, and therefore the model is unable to assess the human health risk (Chowdhury, 2004). Moreover all these models are deterministic models, the arrangement to incorporate the natural and model parameters uncertainty is very limited.

The risk from produced water depends on the distribution of contaminants in the marine environment (Karman and Reerink, 1998). Inclusion of uncertainties in the model parameters and the concentration distributions would provide a better prediction of exposure concentration (EC) than those of a single value output model. USEPA (1997) predicted the fish tissue concentration from a snap shot value of lipid content in fish to be a seasonally variable factor (Madenjian et. al., 2000). Chowdhury (2004) considered the edible part of fish when calculating the fish weight for the risk estimation. The edible part of fish is determined as the summation of flesh, skin and lipid content. Metals, PAHs and other chemicals are bioaccumulated in the edible part of fish and thus may pose a risk to human health.

Metals can bioaccumulate in fish liver and kidneys (Eisler, 2002) and also can migrate between fish tissues (Cambell et. al., 1988). PAHs also tend to have high bioaccumulation effects in the fish tissue (Neff, 2002). Like other vertebrates, fishes have well-developed mixed function oxygenase (MFO) systems that can rapidly metabolise PAHs into hydrophilic products which are more easily excreted and difficult to measure (Perez et al, 2008). Escartin and Porte (2000) measured the higher level of PAHs in bile of red mullet and sea comber in the north-west Mediterranean. Giulio and Hinton (2008) also reported that PAHs exposed marine fish shows potential genomic alterations including oncogene activation.

Literature reviews reveals that, there is no methodology to estimate the human health risk from PAHs accumulation in fish originated from offshore produced water. The adopted methodology by Meinhold and Hamilton (1992) and Chowdhury et al. (2004) only considered the human health risk from naturally occurring radioactive material (NORMs). Chowdhury (2004) estimated the human health through the edible portions of fish ingested by human. He used the Von-Bertalanffy model to model the fish growth. This model works well when analyzing fish populations at the annual level. But in a produced water contaminated area the residency of fish needs to be considered at any particular time. The cited research works also shows that, there is no approach to estimate the effects of several constituents all together. The USEPA (1997) approach provides general values for many risk estimation parameters. Some of these parameters such as fish intake can be highly variable depending on the locality. The exposure frequency as suggested by USEPA (1997) is 350 days/year typically. For North-American food habits, this exposure frequency for fish intake is highly unlikely (Josupeit, 1996) would be so high, and the high estimation may results higher risk estimation. These issues are addressed in the present work.

1.2 Motivation

Atlantic Canada is emerging as a global figure in the oil and gas industry with the development of Hibernia and oil fields. The environmental and other related concerns from the offshore produced water are of greatest concerns among the environmentalist around the world. The variability and uncertainty of the oil and gas field environment requires continuous monitoring, policy formulation and assessment to protect the ecology and human health. The risk estimation of human health is a complex process and a probabilistic approach of the risk assessment can incorporate the uncertainties. Among the other produced water contaminants Polycyclic Aromatic Hydrocarbons (PAHs) special attention due to their toxicity and persistence. Other offshore oil and gas rich areas, like Norway and the UK have tried to minimize the environmental damages for the last couple of decades. With the new prospect in Atlantic Canada, it is a great chance to prepare in advance for any possible risk and hazard and formulate the necessary policies accordingly. The human health risk assessment from produced water for the Canadian lifestyle is a less studied subject yet. The typical standards or procedures may not be a good fit for this region. A survey among the peoples to get the real life information can improve the risk assessment procedure. All of these challenges highly motivate the conduction of this research.

1.3 Objectives and Tasks

The objective of this research is to estimate the human health risk from PAHs of produced water, integrate the risk values with other pollutant such as NORMs, and improve the risk assessment model and parameters.

The proposed methodology in this research will have the following tasks:

- Development of a fish growth model by using the method suitable for produced water exposed area.
- Development of a human health risk assessment model for PAHs using probabilistic approaches.
- Conducting questionnaire survey in the local communities to estimate the fish intake trends.
- Application of the developed methodologies by using data from literature and information from questionnaire survey.
- Comparing the estimated results with ones from the Decision Support System of Produced Water Management (DISSPROWM).

The questionnaire survey was conducted on the different people groups in the St. John's, NL local areas. The risk estimation model was improved by using the parameters from this survey, recent literature review and comparing the results with other published studies. A hypothetical case study was conducted to implement the methodology.

1.4 Organizations

The background of the study is presented in Chapter 1. An extensive literature review on the produced water toxicity on environment and human health is given in Chapter 2. The human health risk assessment methodology and related fish growth model is described in Chapter 3. Chapter 4 presents a case study by using the proposed method and associated questionnaire survey and Chapter 5 summarizes the research findings and future research scopes.

Chapter 2

RISK FROM PRODUCED WATER

2.1 Introduction

Oil and gas reservoirs have a natural water level known as formation water, which lies under the hydrocarbon layers in the reservoirs and is the main source of produced water. The physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geological formation with which the produced water has been in contact for thousands of years, and the type of hydrocarbon product being produced. This produced water can have significant environmental effects, if not treated properly.

Produced water discharge varies from platform to platform depending on the geology of the formation layer and platform locations. In the Gulf of Mexico, the daily production can vary from 3,000 to 32,000 m^3/day (Veil et al., 2005). In the Java Sea, the discharge rate is 123,000 m^3/day (Mukhtasor, 2001). The discharge of produced water from the Norwegian oil and gas industry was 144 million m^3 in 2006 while the total global production was 173 million m^3 (OLF, 2006). Brendehaugh et al. (1992) reported an increase in produced water discharge in the North Sea. In the UK continental shelf, the oil content in the discharged produced water though shows a decreasing trend, but the amount of produced water discharge has an increasing trend. As a result, the total amount of oil discharged into the ocean remains approximately the same from 1991 to 2000 (Data by Design, 2001).

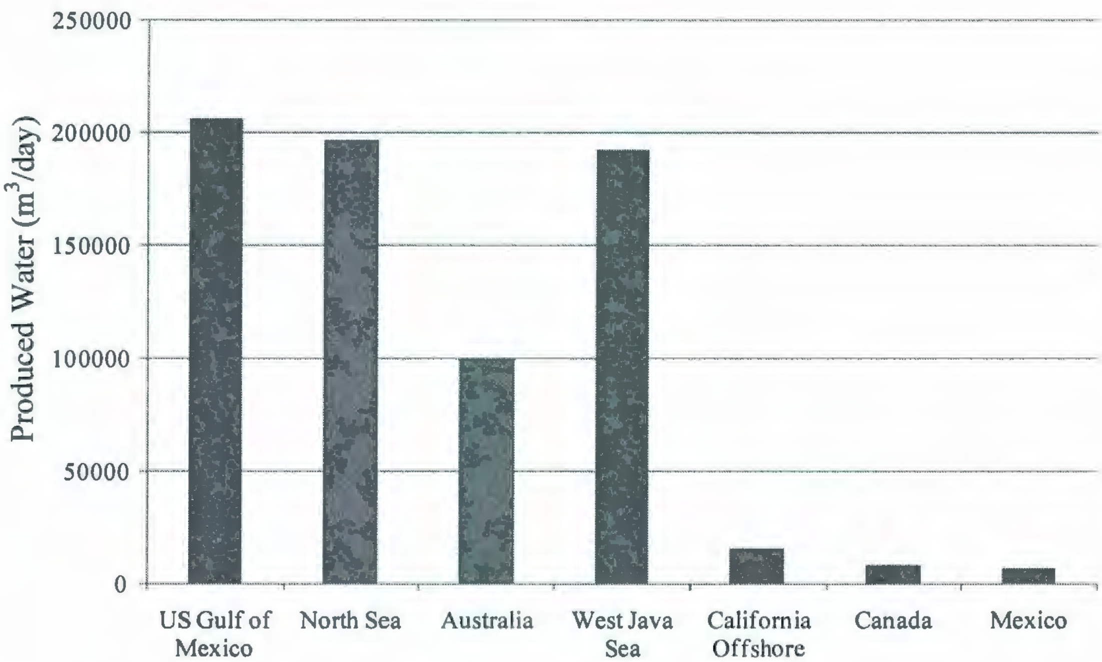

Figure 2.1 Volume of Produced Water Discharged into the Ocean

(Neff and Sauer, 2000 and National Research Committee, 2003)

Figure 2.1 shows the discharged volume of produced water in different regions. The Gulf of Mexico has the highest discharge rate of produced water as shown in the figure. The amount of produced water production with that of oil and gas production were compared for different regions (Karl et. al, 2007; AGA, 2009; Rigzone, 2008; Bopp, 2009), Figure 2.2 shows a comparison of production of oil and produced water in some regions. The production data of Canada was reported as of 1990 in the National Research Study of Canada.

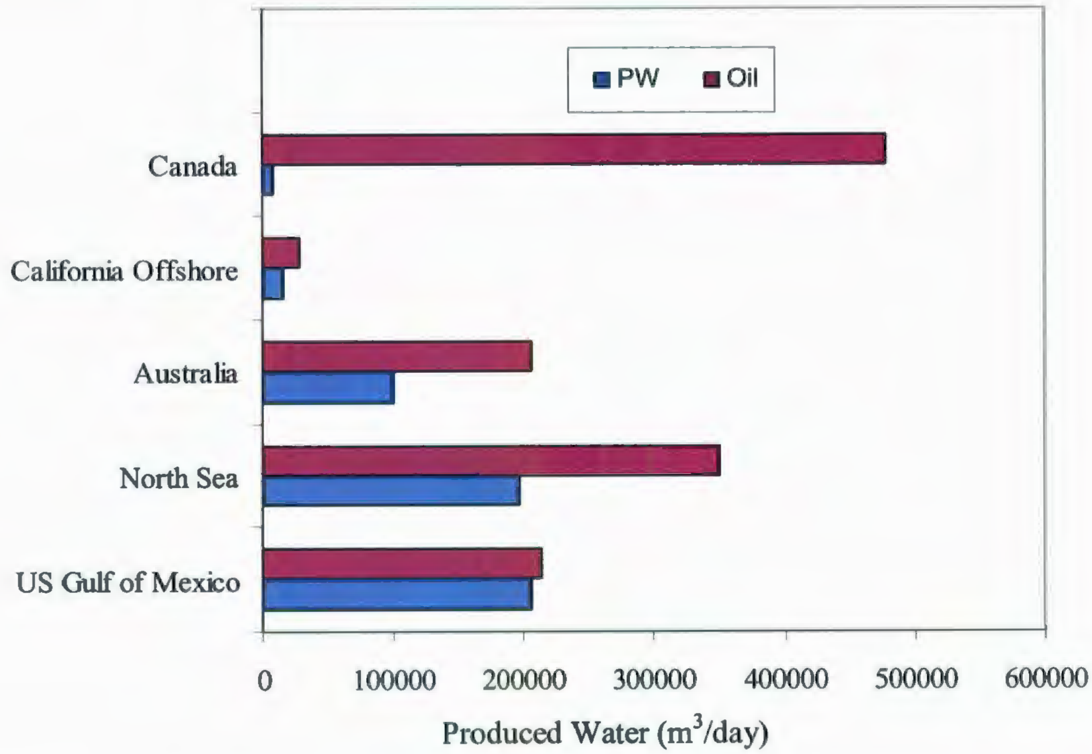

Figure 2.2 Comparison of Oil and Produced Water Production
(Karl et. al, 2007; AGA, 2009; Rigzone, 2008; Bopp, 2009)

In Atlantic Canada, five discoveries have been put into production to date. These are: Hibernia, Terra Nova, White Rose, Coheasset and Sable Island. The Cohasset field was operated from 1992 to 1999, producing a total of 7.1×10^6 m^3 of gas (CAPP, 2001). That project is now decommissioned and environmental follow up will be carried out until 2009. Though the produced water discharge is limited due to smaller activities, it is anticipated to increase as new oil and gas fields are developed in future and the volume of water increases with the age of well. Summary of production of these fields are listed in Table 2.1.

Table 2.1 Atlantic Canada Production Summary Data (C-NLOPB 2008, C-NSOPB 2008)

Field	Total Production			Platform Type	PW Treatment
	Oil ($10^6 m^3$)	Gas ($10^9 m^3$)	Water ($10^6 m^3$)		
Hibernia	7.825	2.071	5.895	Gravity	Hydrocyclone
Terra Nova	6.747	1.477	2.445	FPSO	Lack Information
White Rose	6.806	0.924	2.691	FPSO	Lack Information
Sable Island	N/A	4.40	0.236	Jacket	Hydrocyclone

FPSO- Floating Production, Storage and Offloading

2.2 Priority Pollutants

The composition of produced water depends on whether crude oil or natural gas is being produced and generally includes a mixture of either liquid or gaseous hydrocarbons, produced water, dissolved or suspended solids, produced solids such as sand or silt, and injected fluids and additives that may have been placed in the formation as a result of exploration and production activities. The constituents of concern are those that cause toxic effects and those that impact the ecosystem and its function such as nutrient cycle, the collective intraspecific and interspecific interactions of the biota, flammability etc. Salinity, metals, Phenols, Benzene, Tolune, Ethyl Benzene and Xylenes (BTEX), Polycyclic Aromatic Hydrocarbons (PAHs), Naphthalene, Phenanthrene and Dibenzothiophene (NPD) and their alkyl homologues, naturally occurring radioactive materials (NORM) are considered as the pollutants from produced water.

In US, produced water salinities range from 0.1 to 400 parts per trillion (ppt) (PWS 2008) and most produced waters have salinities greater than the salinity of seawater which is 35 ppt. Most marine organisms can tolerate salinities ranging from 10 to 40 ppt if the ion ratios of the produced water are comparable to those of seawater. A combination of ion ratio different or higher or lower salinity from those in seawater may be an important causative agent of produced water toxicity in marine organisms (Neff, 2002).

Table 2.2 Heavy Metal Concentrations in Produced Water (from CAPP, 2001)

	North Sea (μg/l)	Gulf of Mexico (μg/l)	Canada (μg/l)
Arsenic	0.004-12	<0.11-320	-
Barium	-	1-650,000	-
Cadmium	<0.0005-94	0.068-98	2-6
Chromium	<0.001-11	<0.01-390	80
Copper	<1-100	<0.05-210	8-2,400
Lead	<1-400	<0.08-5,700	8-45
Mercury	0.00001-75	0.06-0.19	-
Nickel	20-95	0.1-1,674	20-420
Zinc	5-35,000	7.3-10,200	90-26,000
Radium 226 (pCi/L)	45	0-1,565	-
Radium 228 (pCi/L)	105	0-1,509	-

pCi/L- Picocuries Per Liter

Depending on the geological formation of the reservoir, produced water may contain metals like Aluminum, Barium, Cadmium, Chromium, Copper, Lead, Iron, Nickel and

Zinc. Their concentrations may vary from 100 to 10,000-fold or more than their concentrations in sea water. Table 2.2 summarizes the amounts of heavy metals available in produced water in the North Sea, Gulf of Mexico and Canadian offshore.

NORMs originate in geological formations and can be brought to the surface with produced water. The most abundant naturally occurring radionuclides are usually radium-226 (^{226}Ra) and radium-228 (^{228}Ra). Concentrations of ^{226}Ra in seawater are in the range of 0.03 to 0.1 pCi/L and ^{228}Ra about 0.005 pCi/L (Neff and Sauer, 2000). The average concentration of ^{226}Ra in the Gulf of Mexico and North Sea varies from 45-226 pCi/L and for ^{228}Ra from 105-278 pCi/L (CAPP, 2001). Marine plants and animals may bioaccumulate radium from solution in the ambient water, from ingested sediments or from their food. Neff (2002) reported that more than 42% of the accumulated radium is deposited in the bone of a fish.

Phenols are a natural ingredients of the ocean, produced from synthesizing and degradation from a wide variety of plants and microbes. Typical concentrations of phenols in produced water from North Sea are in the range of 2-23 mg/L and for Gulf of Mexico 0.20-3.40 mg/L. Phenols can be readily degraded by bacterial and photo-oxidation in seawater and marine sediments and are not considered very toxic to marine organisms. But Neff (2002) reported that toxicity from phenols increase with the taxonomic position of the marine organism.

BTEX concentrations in produced water are usually high but they may not pose a high risk as these compounds evaporate rapidly as soon as they discharge into the marine environment (Furuholt, 1996). After evaporation, they can react with other air pollutants and after broken down may returned to the earth or involved in the formation of photochemical smog (SEPA, 2006). Though these pollution may causes harm to human health directly, there effect of fish population is not well known. there The concentrations of BTEX in produced water range from 68 μg/L to 600,000 μg/L. Benzene is known as a human carcinogen and BTEX compounds are considered to include nonspecific narcosis and alternation of permeability in cell membranes of marine organisms.

PAHs are defined as hydrocarbons containing two or more fused aromatic rings; they are toxic and persistent in the marine environment (Neff and Sauer, 2000). PAHs are the hydrocarbons containing two or more aromatic rings and their concentrations range from 40-3,000 μg/L. The low molecular weight PAHs usually represents more than 95% of the total PAHs in produced water. The aromatic fraction of produced water is dominated by BTEX (Benzene, Toluene, Ethylbenzene and Xylene) and NPD (Napthalene, Pnenanthrene and Dibenzothiophene) and they are highly soluble to water (OGP, 2002). High molecular weight PAHs are less soluble and thereby less harmful to the marine environment. Also the higher molecular weight PAHs are removed mostly from produced water through the treatment process and their impacts are thus reduced. The solubility of PAHs decreases as their size increases (Neff, 2002), so the concerning PAHs are two and three rings PAHs. The BTEX compounds are volatile and will evaporate rapidly from produced water discharged close to the sea surface or from the discharge plume. The NPD though less volatile, will evaporate to some degree also. So, two and three- rings PAHs are expected to associate with particulates and oil droplets in the produced water (Knudsen et al., 2004). Alkyl PAHs are more abundant than their parent compounds and they are more persistent in the environment.

The US EPA shortlisted 16 PAHs according to their toxicity effects and they are considered to be having great environmental concerns. Table 2.3 summarizes the concentrations of these 16 PAHs and their alkyl compounds.

The US EPA express concerns that PAHs could be bioaccumulated to potentially toxic concentrations by marine organisms in the receiving waters of offshore produced water discharges (Neff et. al, 2000). Possible genetic damage has been identified in fish and marine animals from oil spill sites and from the vicinity of industrial wastewater discharges (Wirgin and Waldman, 1998). Napthalene, Benzo(a)pyrene, Benz(a)antharenece etc. are considered to have a carcinogenic effect on human health.

In addition to these naturally occurring chemicals in produced water, process chemicals from corrosion inhibitors, scale inhibitors, emulsion breakers, coagulants, flocculants, clarifiers and solvents etc. may remain in the produced water and are disposed with it. These additives may pose some toxicity to the marine organisms.

Table 2.3 Concentration of PAHs in Produced Water

PAH Compound	Minimum[1] (µg/l)	North Sea[2a] (µg/l)	North Sea[2b] (µg/l)	North Sea[2c] (µg/l)	Mean[3] (µg/l)	Maximum[1] (µg/l)	Classification	
							US EPA[4]	IARC[5]
Naphthalene	194	350	-	530	145	841	D	3
C1- Naphthalenes	309	260	-	420	-	2901	-	-
C2- Naphthalenes	145	150	-	200	-	3207	-	-
C3- Naphthalenes	56	100	-	80	-	2082	-	-
Phenanthrene	9	16.4	-	18.8	13.6	111	D	3
C1- Phenanthrenes	17	20.3	-	18.7	-	323	-	-
C2- Phenanthrenes	14	6.3	-	15.3	-	365	-	-
C3- Phenanthrenes	9	7.9	-	7.4	-	273	-	-
Acenapthylene	0.1	2.2	2.16	-	0.86	6.1	D	N/A
Acenapthene	0.3	1.8	1.63	1.5	2.0	15.3	N/A	N/A
Fluorene	4.1	8.9	6.15	15.4	-	66.7	N/A	3
Anthracene	0.1	-	1.08	-	-	2.6	D	3
Fluoranthene	0.1	0.4	0.27	1.7	0.26	3.6	D	3
Pyrene	0.2	0.7	0.43	5.1	0.63	7.7	D	3
Benz(a)anthracene	0.1	0.6	0.23	2.0	0.23	2.8	B2	2A
Chrysene	0.6	0.5	0.48	-	0.84	15.2	B2	3
Benzo(b)fluoranthene	0.1	-	0.03	-	0.028	3.4	B2	2B
Benzo(k)fluoranthene	0.0	0.2	0.01	0.7	0.007	0.6	B2	2B
Benzo(a)pyrene	0.0	0.2	0.02	-	0.63	1.1	B2	2A
Indeno(1,2,3-c,d)pyrene	0.0	-	0.01	-	0.005	0.4	B2	2B
Dibenz(a,h)anthracene	0.0	-	-	-	0.005	1.2	B2	N/A
Benzo(g,h,i)perylene	0.0	0.2	0.01	-	0.029	2.7	N/A	3

[1]OGP, 2002; [2a] Utvik et al., 1999, Ekins et al,, 2005, [2c]Utvik, 1999; [3]OGP. 2005
[4]U.S. Environmental Protection Agency: B2: Probable human carcinogen; D: Not classifiable
[5]International Agency for Research on Cancer: 2A: Probable human carcinogen; 2B: Possible human carcinogen; 3: Not classifiable; N/A - Not available

2.3 Physical Transport of Produced Water

To assess the impacts of the produced water constituents when they discharge to the sea, it is necessary to consider the fate and transport mechanisms of each components and how they vary with time. The fates of these chemicals are determined by dilution, volatilization, chemical reaction, adsorption and biodegradation. The transport mechanisms and pathways for the individual chemicals are different.

After it is discharged, the plume of produced water will descend or ascend depending on its relative density to the ambient seawater, and it will bend in the direction of the ambient current until it encounters the seafloor or reaches the water surface. During the near-field phase, the plume will usually be trapped at a neutrally buoyant level before it encounters the seafloor or reaches the water surface. This phase ends within minutes and within a few meters from the discharge.

After the near-field phase, the plume reaches the produced water and seawater boundary and it spreads as a thin layer. In this phase, mixing is dominated by buoyant spreading and oceanic turbulent diffusion mechanisms. Both of these mechanisms could be important over a distance from the discharge point, but as the plume travels downstream, the buoyancy effect decreases and the turbulent effect increases.

2.4 Fate of Chemicals in Produced Water

After discharge to the seawater, produced water salinities are likely to change rapidly toward that of the ambient water. Smith et al. (1996) showed that 100-fold dilution occurs within 10 m of the discharge, which reaches to 1,000-fold within 103 m of the discharge.

The metals of produced water are diluted rapidly in the receiving environment upon discharge. Barium will precipitate as barium sulfate in the presence of a high natural concentration of sulfate in sea water. Iron, Manganese and Aluminum in produced water can generate inorganic metal oxide precipitates at 20-50 mg/L concentrations on release into aerobic seawater which may flocculate (a process where a solute comes out of solution in the form of floc or flakes) to form aggregates which may facilitate the rapid transport of toxic produced water constituents to the benthic environments. Elevated concentrations of co-precipitating metals and residual hydrocarbons may occur within the surface micro-layer due to the attachment of precipitates to buoyant oil droplets. Arsenic from produced water dilutes very rapidly in the receiving water environment.

The NORM of produced water is rapidly co-precipitated with barium sulfate. Small amounts of radium may accumulate in sediments near produced water discharges to shallow, poorly-mixed coastal waters.

Phenols and alkyl phenols present in produced water are diluted rapidly into the sea water. Phenols are not persistent in marine environments. They go into aqueous solution readily but evaporate from water. Riksheim and Johnsen (1994) concluded that the dilution factor was 10,000:1 for phenols at 10 m downstream of the discharge point. Phenols are also rapidly degraded by resident bacteria and by photolysis. Upon discharge, the combined dilution, microbiological activity and photo-degradation and evaporation remove phenols from the water column rapidly (Neff, 2002).

BTEX compounds are very volatile and evaporate rapidly from the water after discharge. They are also biodegradable under aerobic conditions but the degradation rates are much slower than evaporation. Photo oxidation of BTEX compounds in water may contribute to the disappearance of these compounds from the water column.

PAHs in produced water dilute rapidly. PAHs undergo several reactions upon discharging to solar radiation and produce a variety of polar organic compounds. High molecular weight compounds are not soluble in water or oil and they may accumulate in marine organisms. The microbial degradation of PAHs depends on the molecular weight of PAHs and the ambient environment.

2.5 Risks from Produced Water

In recent years, risk assessment has been integrated frequently as one of the essential processes for sound environmental management. Produced water may pose risk to the marine ecology and subsequent risk to the human health. An ecological risk assessment integrates measured or estimated levels of exposure to a chemical contaminant and measured or predicted injury to valued ecosystem components to characterize the risk (potential hazard) of the chemical to natural populations of the valued ecosystem components. Most frameworks for ecological risk assessment include four stages: i) problem formulation; ii) characterization of exposure; iii) characterization of effects; and iv) risk characterization. The main contributors to acute toxicity (short-term effects) of produced water have been found to be the aromatic and phenol fractions of the dissolved hydrocarbons (Frost et al., 1998). Neff et al. (2006) showed that among the PAH chemicals of produced water, 2- and 3-ring PAHs are the main contributors to the ecological risk of produced water discharges. Actual impacts will depend on the biological effect such as toxicity, bioaccumulation, and oxygen depletion of the produced water at the concentrations that exist over the exposure times found in the environment (Cline, 1998).

A health risk assessment for an environmental pollutant describes the discharge of the contaminant, its transport and fate in the environment, and the resulting human exposure. Human-health risks are then calculated based on data and models that relate exposures to health effects. Produced water discharge from offshore platforms may pose a human health risk through seafood ingestion (US EPA, 2000; Sadiq, 2001). Meinhold et al. (1996) predicted elevated risk from radium ingestion in fish for produced water discharges in the Open Bay, Louisiana. The estimated lifetime cancer risks were found to be less than 10^{-5} for consumption of fishes caught near shallow water platforms and less than $3x10^{-7}$ for consumption of fishes caught near deep water platforms. Meinhold and Hamilton (1992) and Chowdhury et al. (2004) calculated the risk associated from naturally occurring radioactive chemicals of produced water.

Risk estimation always incorporates uncertainties due to the nature of the data and model uncertainty. Probabilistic techniques are used by many researchers to deal with this uncertainty. It helps the decision makers to get a range of values, which is useful from a management point of view.

Risk assessment is the estimation for any stressor that may cause harm to a selected endpoint that has environmental or economical importance. Produced water is generated during the extraction of oil and/or gas. It includes formation water, injected water, small volumes of condensed water, and any chemicals added during the oil/water separation process (US EPA, 1993). Each year, 6.91 million m^3 of produced water is discharged to surface waters from the offshore industry (Wiedeman, 1996). Produced water contains several potential toxic metals, small amounts of radionuclides, as well as industrial additives (DFO, 2001). These waters are treated to satisfy regulatory standards prior to discharge into surface waters. Regardless of the treatment, produced water may contain chemicals that are of environmental concern. There is a concern that the produced water discharge may be causing contamination of the marine system ecology by affecting fish and fish habitats (DFO, 2001).

Produced water toxicity and its environmental effect has been of great interest in many recent research studies (Kungolos et. al, 2006; Scott et. al, 2005; Niaz et al., 2009, Sundt et. al., 2009). Most toxicity tests have been conducted to determine the short-term, acute toxicity of produced waters discharged to marine waters. Despite the variations of produced water compositions research findings indicate that causative toxicants can be identified. As produced water are discharged to the sea the concerns of possible negative environmental effects have been of great interest in the scientific community. Studies have focused a broad diversity of habitats and a variety of marine invertebrates and vertebrates. Due to year-to-year natural variability, the cause and effects of produced water compounds on the general fish stock is not well investigated yet.

In Atlantic Canada with the development of Canada's offshore oil and gas reserves, produced water is of concern to regulators and the environmental community.

2.5.1 Ecological Risk Assessment

The term of ecological risk assessment (ERA) is typically defined as 'a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors (US EPA, 1998). The purpose of ERA is to contribute to the protection and management of the environment through scientifically credible evaluation of the ecological effects of man-made activities such as disposal of wastes from offshore oil production (Mukhtasor, 2001). In the last two decades, interest in ecological risk assessment has increased significantly and guidelines for the assessment have been made available from regulatory agencies.

Risk assessment is conducted to translate scientific data into meaningful information about the risk of human activities to the site-specific environment. The ERA framework by the US EPA allows risk managers to make informed environmental decisions (US EPA, 1998). Different management options for produced water were evaluated in many studies in order make the decision support system more user friendly (Lawrence et al., 1993; Evans, 2001).

For the assessment of risk there are several established methods provided by different organizations. The National Research Council of the National Academy of Sciences (NRC-NAS) (1992) model, US EPA model (1998), Council of Ministers of the

Environment (CCME) model (1996) and Water Environment Research Foundation (WERF) model are prominent of these.

Figure 2.3 shows details of these models. The NRC-NAS model was first published in 1983 to identify the risk and quantify the degree of risk to individuals and population as a whole (NRC, 1996).

US EPA provides a comprehensive model for ERA (US EPA, 1998). There are four basis steps in this model, which are i) Problem formulation, ii) Analysis, iii) Risk characterization, and iv) Risk management and communication. Problem formulation combines a) assessment endpoints, b) conceptual models and c) analysis plans.

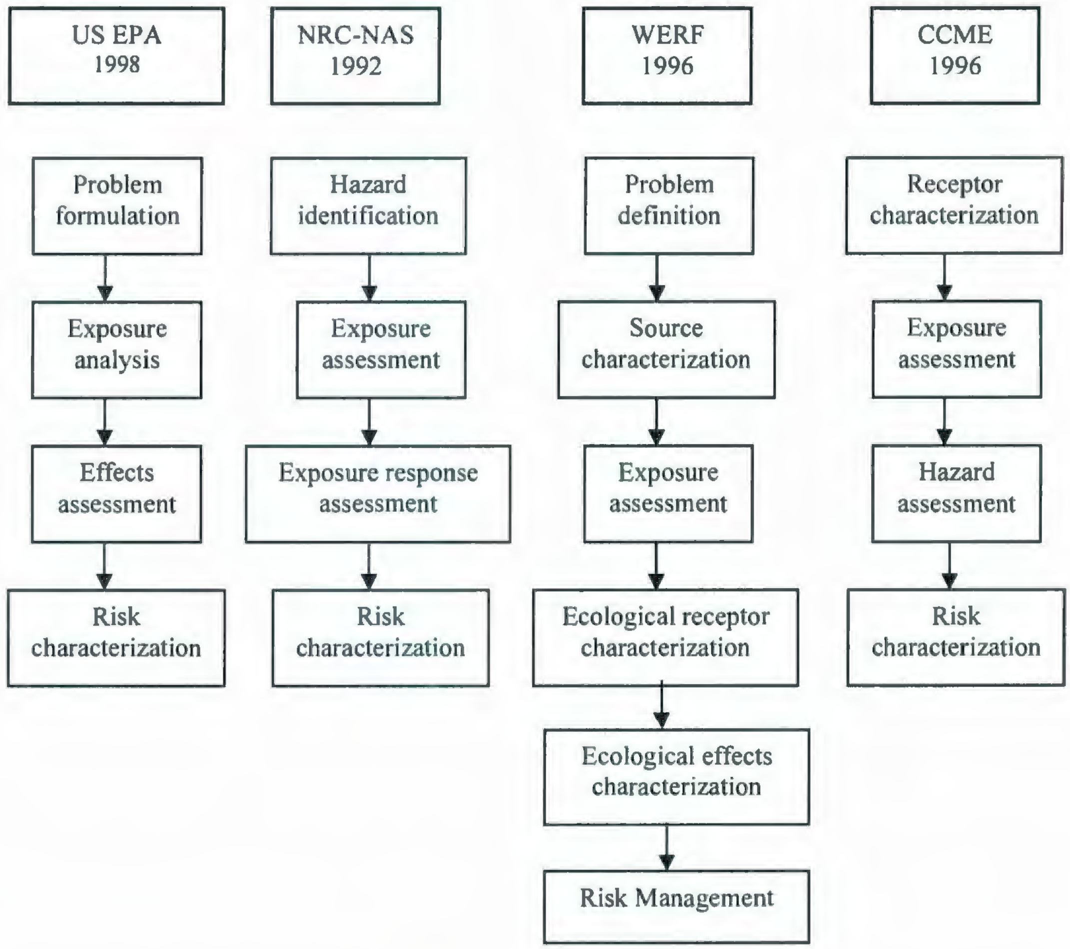

Figure 2.3 Ecological Risk Assessment Frameworks (US EPA, 1998; NRC-NAS, 1992; WERF, 1996; CCME, 1996)

The risk assessment process includes the use of measurement, testing and mathematical modeling to quantify the relationship between the initiating event and possible adverse effects (Suter, 1993). The ERA method is used to interpret dose-response data into a risk assessment by application of the response information to local site-specific pathways and biota. There are three phases to the ERA process. The first phase is problem formulation.

Problem formulation is used to evaluate a preliminary hypothesis about the possible ecological effects from human activities. The second phase of the assessment is the analysis phase that considers the two primary components of risk assessment (i.e.- exposure and effects). The third component of the ERA process is the characterization of the ecological response and the quantitative estimation of risk.

Numerous studies on ecological risk assessment have been carried out to assess the ecological risk from produced water (Brendehaug et al., 1992; Stagg et al., 1996; Neff and Sauer, 2000; Booman and Foyn, 1996; Neff, 2002, Neff et al. 2006). Considerable research has also been conducted in characterizing ecological risks from produced water contaminants (Ray and Engelhardt, 1992; Reed et al., 1996; Neff et al., 2006). Addressing the ecological impact, several regulatory agencies set different discharge criteria for the oil content of produced water in different regions (C-NOPB, US EPA, MMS, OSPAR).

OGP (2002) reported that, no significant effects were detected from chronic exposure to produced water by the cages fish. Several EC_{50} (concentration that restricts growth of 50% of the exposed population) and LC_{50} (concentration that kills 50% of the exposed population) values for different marine species were reported for produced water by Holdway (2002) and Neff (2002) as a percent of total oil in produced water. Neff et al. (2006) concluded that risk from PAHs in produced water was minimal. Change in respiration rates has been observed in fish eggs and larvae exposed to benzene (Eldridge et al., 1977), one of the most abundant contaminants in produced water. No effects on oxygen consumption rates to yolk-sac larvae was detected with 25 μg/l, 100 μg/l or 500 μg/l phenol concentration for a 2-day exposure scenario, but for 5-day exposure, effects on oxygen consumption were detected at 25 μg/l and 100 μg/l concentrations respectively (Booman and Foyn, 1996). They determined the 24-hour LC_{50} as 7 mg/l BTX (mixture of benzene, toluene and xylenes) for adult Crustaceans (*Calanus spp.*) and over 5.6 mg/l for naupliar stages. Very rapid dilution occurs in volatile components of produced water and the volatile components fall below the criteria limit with a short distance from the discharge point (Neff and Sauer, 2000). Karman et al. (1996) performed a quantitative risk assessment for the Statfjord and Gullfaks oil fields.

The organic components of produced water include three different types of oil: dispersed, dissolved and free (Yang and Tulloch, 2002). Dispersed oil refers to small droplets suspended in an aqueous phase. The components of dissolved or soluble oil (organic acids, polycyclic aromatic hydrocarbons, phenols and volatiles) are not readily removed from produced water and contribute to its toxicity (Veil et al., 2005). Free oil is oil separate from the aqueous phase. The dispersed and soluble oils not removed by the treatment process are usually discharged into the ocean; free oil is usually removed (C-NSOPB, 2008).

Produced water pollutants may be present in surface water at very low concentrations, but some of them bioaccumulate in aquatic organisms through the food chain and accumulate at a much higher level than in the water itself. The persistent chemicals have more tendencies to bioaccumulate and are considered more toxic for marine lives.

Small fish and zooplankton eat large quantities of phytoplankton, thus any toxic chemicals accumulated in phytoplankton are accumulated in smaller fishes. This is repeated in each of the steps of the food chain, thus the concentrations in the top predators, such as bigger fish can be millions of times higher than the ones in water (LaMP, 2009). The toxic endpoints used for fish risk estimation are subtle and some of the effects may be caused by other factors such as the normal aging process. Health Canada (2007) conducted a detailed report on human health risk from consuming mercury contaminated fish from freshwater and they propose a maximum daily intake rate to avoid the risk. The global climate changes and human activities are also creating a great concern for marine lives, which in turn will effect to human health (Fleming et al., 2006).

When calculating human health risk from fish, fish ingestion rate is an important factor. The US EPA suggested fish intake rate is accepted and used commonly for human health risk estimation. The US EPA suggested to consider the concentration only in the edible part of the fish and shellfish. The US EPA 95th percentile value of fish intake is 132 g/day (US EPA, 1991). The upper 95th percentile fish ingestion rate of 170 g/day was recommended for Native American subsistence populations by US EPA (1996). For human health risk assessment US EPA (1999) used the 99th percentile fish consumption rate of 177g/day. This fish ingestion rate may be highly variable depending on the region. Also the US EPA recommended value is a generic one rather than the marine fishes only. In Atlantic Canada there are no such fish ingestion rate data available in the literature.

2.5.2 Human Health Risk Assessment

A human health risk assessment for a pollutant describes its discharge, transport and fate in the environment, and the resulting human exposure. Human health risks are then calculated using data and models that relate exposures to health effects (Meinhold et al., 1996). With the growing concern of ecological risk from produced water, concerns are growing for human health risk from the produced water pollution.

Produced water discharges from offshore platforms may pose a human health risk through seafood ingestion. Certain types of contaminants discharged from offshore operations may be accumulated in the fish tissues and thereby pose a risk to human health (Sadiq, 2001; US EPA, 2000). Meinhold and Hamilton (1992), Meinhold et al. (1996), Chowdhury et al. (2004) predicted the human health risk from radium, a radioactive contaminant in produced water.

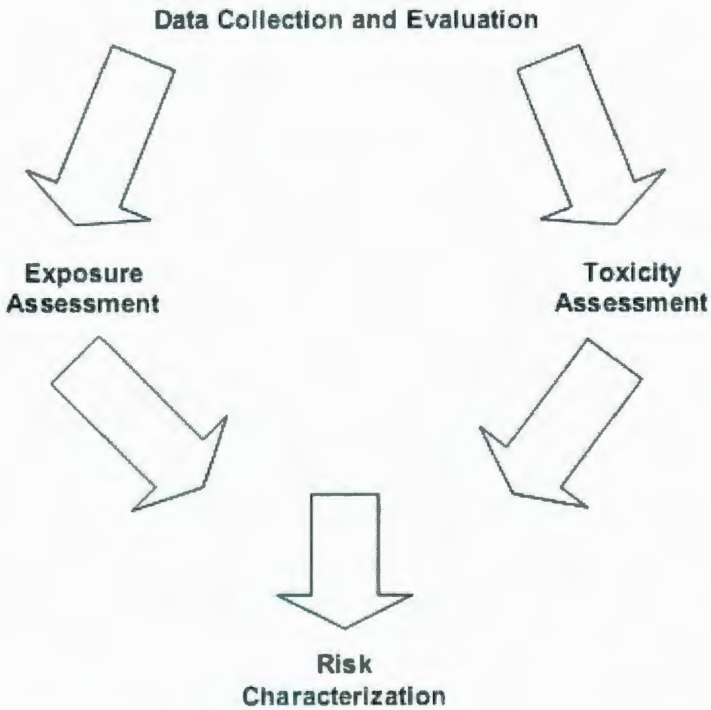

Figure 2.4 Human Health Risk Assessment Frameworks (US EPA, 1999)

As discussed in the previous sections, though ERA has several different models; for human health risk estimation a general approach usually adopted as shown in the Figure 2.4 (US EPA, 1999). The exposure is the most complex step for human health risk assessment, as direct field data are not readily available. For quantitative human health risk assessment Health Canada suggested the following steps (Kathryn et al., 2004):

- Collection of contaminated samples
- Data collection and statistical analysis
- Modeling by using the data

- Characterization of the contaminated sites and receptors
- And, risk characterization

By incorporating the US EPA framework and these steps, any risk assessment model can be developed for human health risk.

Human health risk assessment estimates rely on parameters such as environmental concentrations, body weight, absorption by the body, exposure scenario and several other parameters, and each of these parameters can differ from one site to another. Two measures are commonly used to describe the probability that harm will result from exposure to a risk agent: i) individual lifetime cancer risk—the estimated increase in probability that an individual will experience a specific adverse health effect as a result of exposure to a risk agent over a lifetime; and ii) population risk—the estimated number of deaths in the exposed population (Meinhold et al., 1992). The results of a risk assessment are used by risk managers to determine the need for regulation or remediation, and to set discharge limits.

2.6 Regulatory Limitations of Produced Water Discharge

The regulatory limitations of oil content with discharged produced water are different for different regions. The regulations for the North Sea, the Baltic Ocean and the northeast Atlantic Ocean are the result of a treaty organization, the OSPAR Commission. In USA, the US EPA are overlooking the regulations for offshore produced water discharges. In Atlantic Canada, the Canada-Newfoundland Offshore Petroleum Board (C-NLOPB) is the regulatory body for the discharge limits.

OSPAR regulations set limits on oil discharged, but they give emphasis on controlling the total amount going into a particular water body not the individual pollutant concentrations (Orszulik, 2007). The US EPA limits oil in produced water as an indicator of toxic pollutants but not for the potential harm caused by the oil itself (Orszulik, 2007). The Arabian Gulf Countries (Bahrain, Iran, Iraq, Kuwait, Oman, Qatar, Saudi Arabia, and United Arab Emirates) have developed the Regional Organization for Protection of the Marine Environment (ROPME), similar to OSPAR but included a couple of regulations from the US EPA regulations. A Summary of the main regulatory limits are presented in Table 2.4.

Table 2.4: Summary of Produced Water Discharge Regulations
(OSPAR, 2007; US EPA, 2003; C-NLOPB, 2008)

Organizations/Regions	Regulations
OSPAR	Discharged oil: Produced water ratio must not exceed 30 ml/l
US EPA	24 hrs average: 42 ml/l, 30 days average: 29 ml/l
Canada	24 hrs average: 60 ml/l, 30 days average: 40 ml/l

2.7 Summary

In this chapter, the characteristics of offshore produced water have been discussed. The priority pollutants from produced water were highlighted and the reasons for selecting PAHs for this study were emphasized. The physical fate and dispersion of the produced water were briefly discussed. The risks associated from offshore produced water to the environment and human health have been discussed along with the risk assessment frameworks. The PAH concentrations and risk framework are used in the following chapters to establish the risk model.

Chapter 3

DEVELOPMENT OF A RISK ASSESSMENT MODEL

3.1 Introduction

Offshore as well as onshore produced water pollutants can be transported to the human body through ingestion of marine organisms such as fish and shrimp. Some of these contaminants may accumulate in the human body in different organs or tissues and can pose a human health risk. Pollutant exposure in fish depends on many factors such as fish type, growth rate, migratory characteristics, sensitivity of fish, food availability and seasonal variation (C&RD, 2004). Marine fishes are migratory in nature and can live in the contaminated area for a substantial amount of their growth lifetime. Kohler et al. (1986) reported a significant change in contaminants in flounder during different times of the year.

The US EPA risk assessment for human health also is in a very general form and needs specific adjustment to calculate the risk from the produced water pollutant. In this chapter, an approach to develop the risk assessment model is considered. In the field of human health risk assessment from produced water, previous works concentrate on deterministic and probabilistic models using the toxicological data of different contaminants. To characterize the human health risk from PAHs, there has been no model used so far. In this study, a methodology is proposed to assess the risk from PAHs from produced water. The researchers estimated the model parameter values according to US EPA standards. In this study a questionnaire survey was conducted to estimate the model parameters to make the model more flexible with the regional conditions. Concentrations of pollutants in the edible portions of fish and their subsequent ingestion in the human body were considered. To capture the uncertainty, probabilistic analysis were used for the model parameters.

3.2 Risk Assessment Model

The application of the fish growth model for human health risk assessment from NORMs was first applied by Chowdhury et al. (2004). In that approach the authors used the Von Bertalanffy growth (VBG) Equations to develop an age-weight model of fish. Though VBG is a widely used fish growth model, for irreversible growth (an increase in cell numbers by cell division), the Gompertz model showed better estimates in the studies as mentioned by Bardos (2006), Forni et. al. (2009) and Lawrence (2001). Katsanevakis and Christos (2008) reported that in many cases the VBG model is not supported by the data and many species seems to follow different growth trajectories. In these studies, field data were compared and fitted into model, for a region or species and then that model was verified by using more field data. In this study, the fish growth model is considered by using both the VGB and Gompertz models to get a better estimation of the growth.

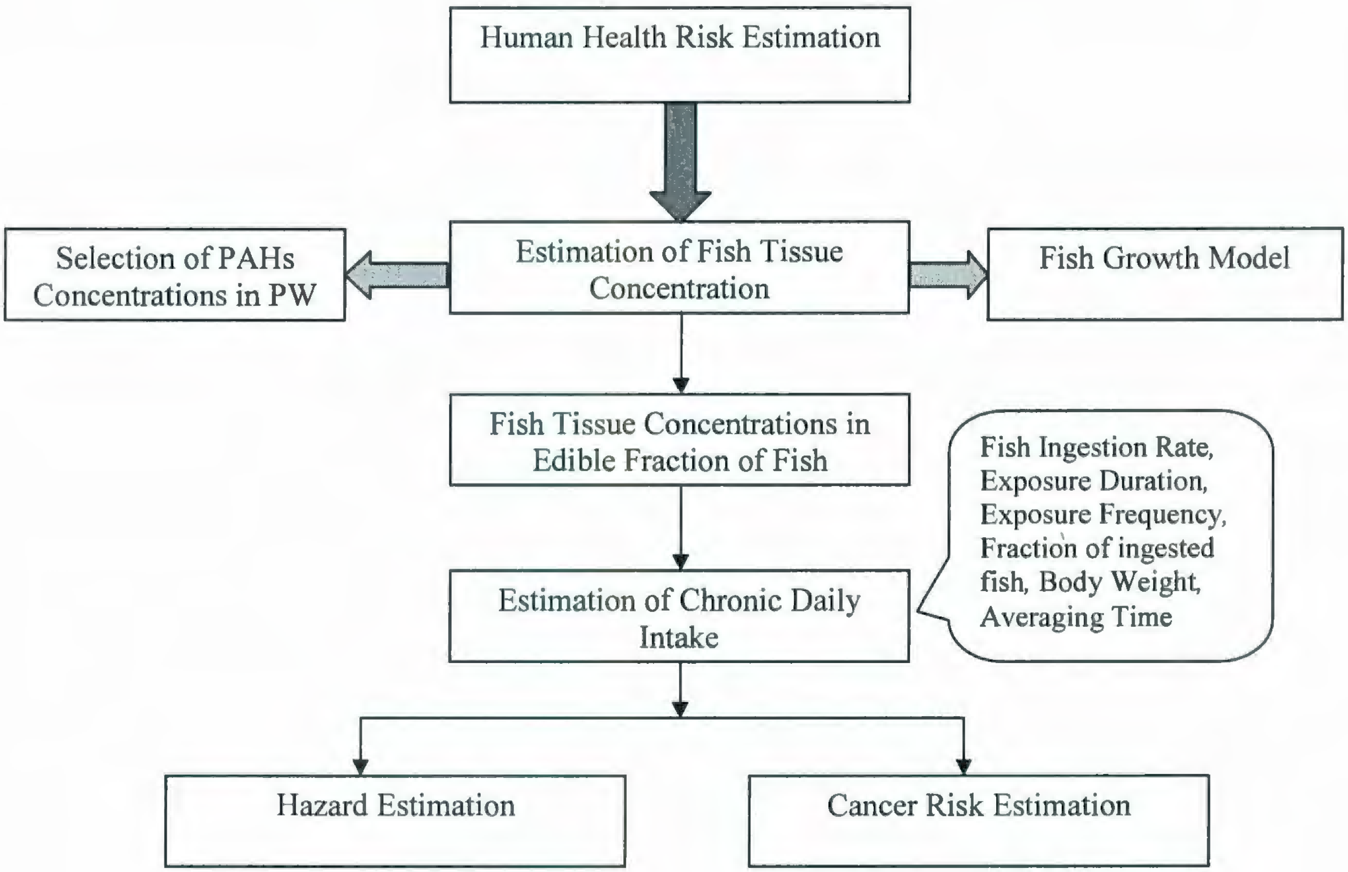

Figure 3.1 Hazard and Risk Estimation Model

The human health hazard and risk estimation methodology applied in this study is described in Figure 3.1. First, among the PAH pollutants, the priority PAH pollutants are selected. Their concentrations and toxicity values were collected from the published literature. Fish tissue concentrations were then calculated by using two different fish growth models: the von Bertalanffy growth model (VBGM) and the Gompertz model. The fish tissue concentration is then used to calculate the human ingestion rate, considering the oral ingestion through food web chain.

3.3 Fish Growth Model

Fish growth models provide a conceptual link between fish growth and an extended framework that includes more biological details in the population dynamics. The dynamic growth of fishes has many implementations and applications in the management of fisheries and many ecological and practical insights can be gained by examining patterns in fish growth (Walters and Wilderbuer, 2000). The effects of environmental factors on growth can be examined through both experimental manipulation and observational studies. But as it is often not feasible to conduct the experimental studies on a specific species, a time series observations of size-at-age and environmental factors are examined (Emily et al., 2003).

Length and weight data are a useful and standard result of fish sampling programs. These data are needed to estimate growth rates, length and age structures, and other components of fish population dynamics (Kolher et al., 1995). There is numerous information regarding the fish growth model in the literature. The decision about which growth model to use is important, as most models deal with transfer of energy along the tropic chain (Gamito, 1998). Growth can be constant or change during developmental periods.

Although initial and final weights estimated with different models may be similar, growth curves as well as the total amount of energy or matter consumed over time may vary considerably during the growth period. It is suggested that the Gompertz growth models are more appropriate for the description of young fish growth and for older fish the von Bertalanffy Equation or some modified form adjusted to seasonal change is preferable (Gamito, 1998).

The most studied and commonly applied model among all the length–age models is the Von Bertalanffy growth model (VBGM) (Katsanevakis and Christos, 2008). Other commonly used alternatives are the generalized VBGM (Pauly, 1979), the Gompertz growth model (Shklovskii, 2005), the logistic model (Xiao et al., 2004), and the Schnute–Richards model (Schnute and Richards, 1990). The VBGM has often used to describe fish growth and is widely used for fish growth modeling, but small sample size can cause poor parameter estimation (Carrier et al., 2004),

In this study a set of three-candidate models was used to model fish growth: VBGM, Gompertz, and logistic. The von Bertalanffy growth model (VBGM) is widely used in the research areas and has been shown to conform to the observed growth of most fish species (Miller et al., 2000). The underlying principle of the VBGM is that the growth rate of fish tends to decrease linearly with size, as indicated in the Equation 3.1.

$$\frac{dl}{dt} = k(L_\infty - L) \qquad (3.1)$$

where,

$L\infty$ = asymptotic length at an infinitely long period

k = relative growth rate parameter (1/yr)

By integrating Equation 3.1 the general form of the VBGM becomes,

$$L_t = L_\infty[1 - e^{-k(t-t_0)}] \qquad (3.2)$$

where,

L_t = length of fish at age t (yr)

t = age in yr

t_0 = the age when an individual fish would have been of zero length assuming the Equation to be valid at all ages

The asymptotic length of fish, $L\infty$ is a hypothetical length at an infinite age. It depends on types of species, availability of food, physical parameters and other environmental conditions. The curvature parameter, k determines how fast the fish approaches to its maximum length. For relatively small fish k values are usually large and for that reason, within a short life span, they reach their maximum length. The initial condition parameter, t_0 is the hypothetical age when a fish has zero length (calculated as the length when age of fish, t=0).

Figure 3.2 shows the growth of *Yellowfin Tuna* according to the VBGM for different values of k. For higher k values, the growth curve reaches to peak sooner. Table 3.1 shows the maximum length (L_{max}), k and t_0 of different fish species.

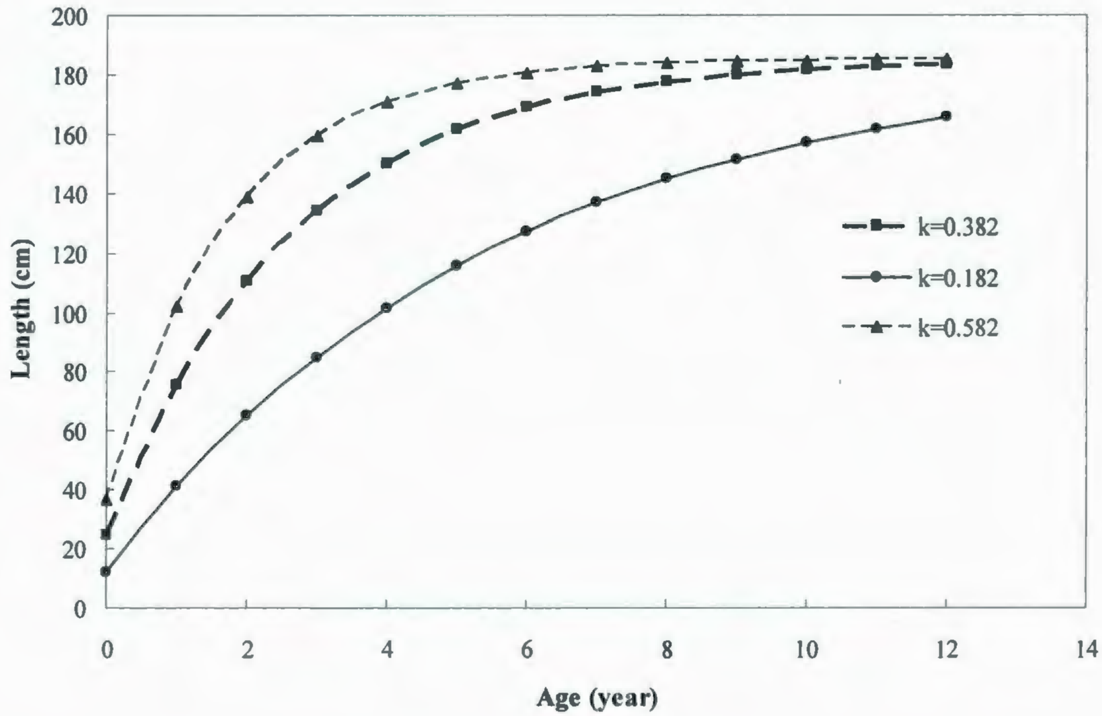

Figure 3.2 Effect of k on age-length relationship for *Yellowfin Tuna* according to VBGM (Fishbase, 2008; USDOC, 2007)

The Gompertz growth model is a sigmoidal growth curve that assumes exponential decrease of the growth rate with size and is given by the Equation 3.3 (Katsanevakis, 2006).

$$\frac{dL}{dt} = \lambda e^{-kt} L \qquad (3.3)$$

where,

λ = theoretical initial relative growth rate at zero age (1/yr)

k = the rate of exponential decrease of the relative growth rate with age (1/yr)

A common parameterization of the solution of Equation 3.3 is:

$$L_t = L_\alpha \exp[-(1/k)e^{-k(t-t_0)}] \qquad (3.4)$$

where, L_t, L_∞, t and t_0 denotes the same meaning as before.

The graphical forms of these Equations were checked by using the data of popular North American fish, *Yellowfin Tuna*. Figure 3.3 represents the Equation 3.4 for *Yellowfin Tuna* fish for different values of k. The figure shows that length of the fish (vertical axis) is proportional to the growth rate. It also shows that in the first two years of a fish life, the growth is most prominent.

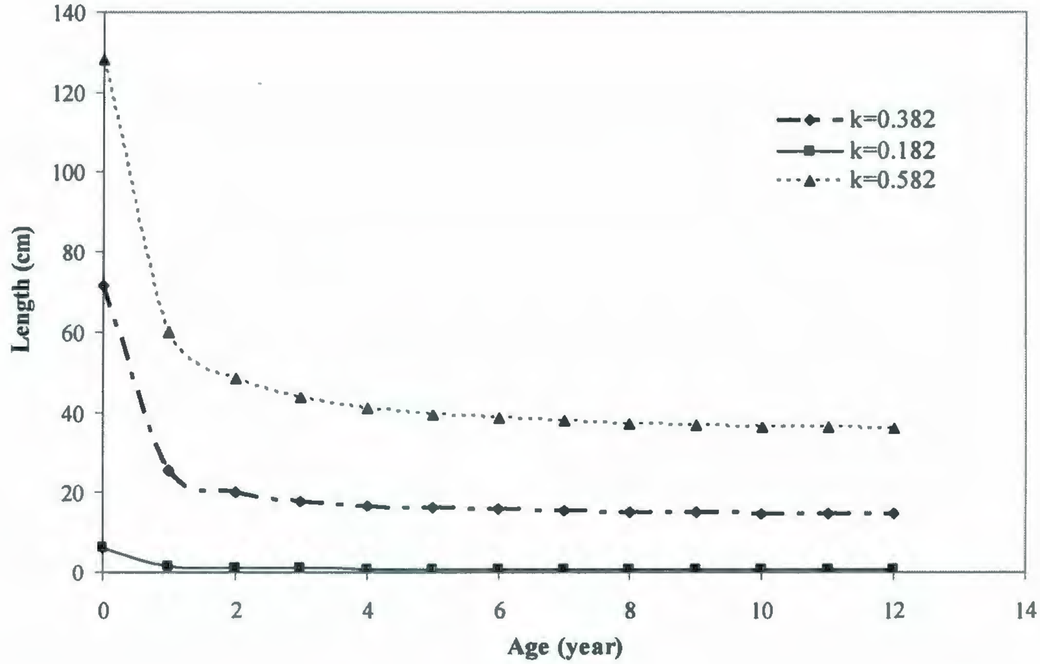

Figure 3.3 Effect of *k* on age-length relationship for *Yellowfin Tuna* according to Gompertz model (Fishbase, 2008; USDOC, 2007)

The parameters of the fish growth model can be estimated in several ways. The Ford-Walford plot is the most commonly used method to estimate those parameters (Pauly et al., 1984). This plot can be useful to help estimate initial parameters for nonlinear regression. Marked on the plot is the 45 degree line and the best fit through the observed points as found by the least squares method. The point where these two lines intersect is an estimate of L_∞ (asymptotic length at an infinitely long period). For Yellowfin tuna the Ford-Walford graph can be estimated as shown in Figure 3.4. Data for this graph were derived from the modified form of the VBGM.

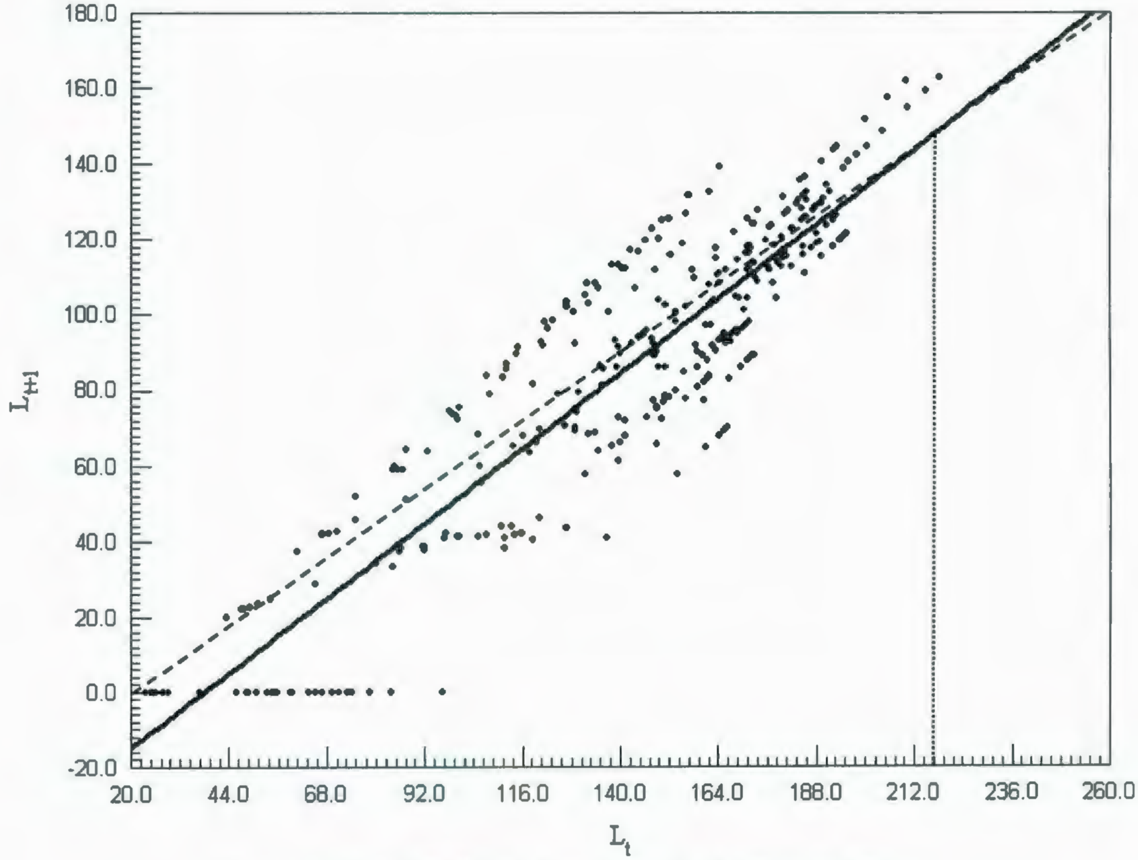

Figure 3.4 Ford-Wilford Graph for the Yellowfin Tuna
(Fishbase, 2008; USDOC, 2007)

Assuming t_0=0, Equation 3.2 can be re-written as,

$$L_t = L_\infty[1 - e^{-kt}]$$

$$=> L_t = L_\infty - L_\infty e^{-kt}$$

$$=> L_\infty - L_t = L_\infty e^{-kt} \qquad (3.5)$$

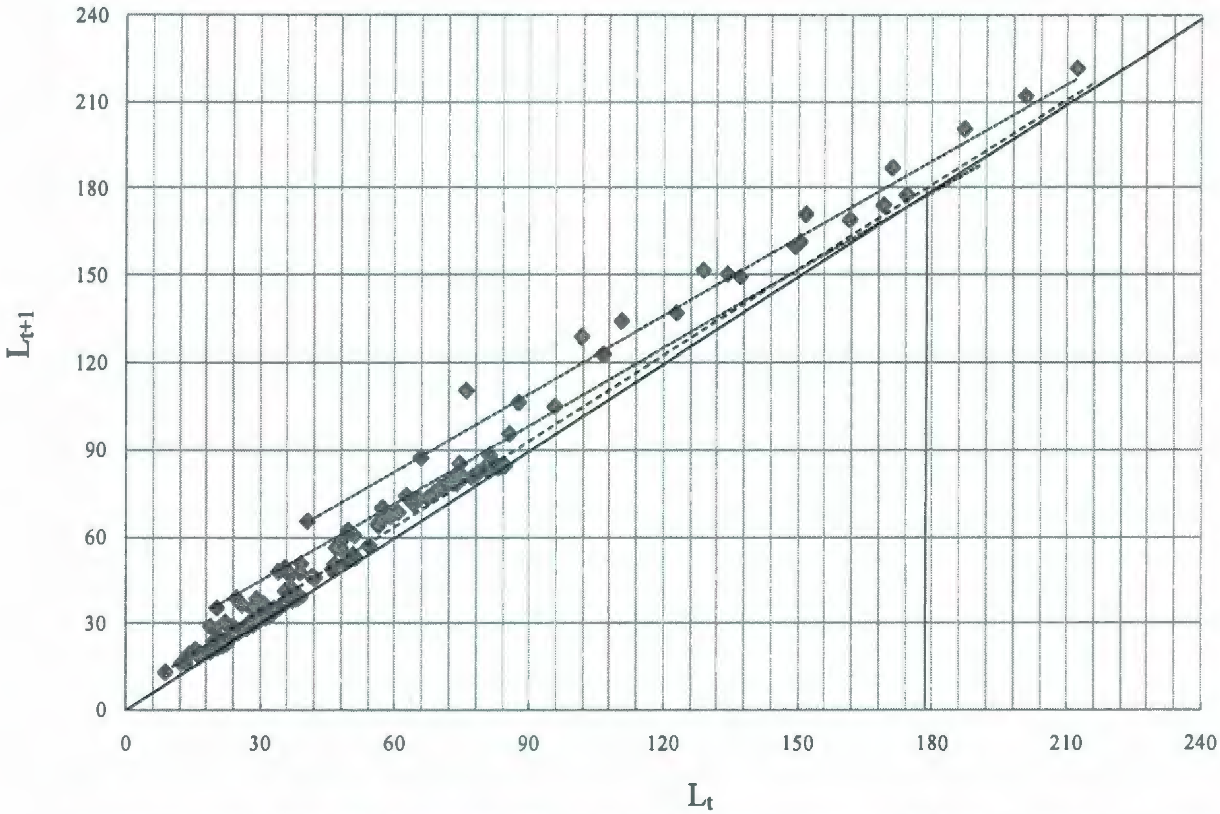

Figure 3.5 Ford-Walford Graphs for the VBG Model (Fishbase, 2008 and USDOC, 2007)

Now substituting, L_{t+1} for L_t in Equation 3.5 and re-writing it, we have,

$$L_{t+1} = L_{\infty}[1 - e^{-k}] + L_t e^{-k} \qquad (3.6)$$

L_{t+1} from Equation 3.6 can be plotted against L_t from Equation 3.2 or 3.4 to fit the data in the Ford-Walford plot.

By using the data in Table 3.1 the Ford-Walford graphs can be drawn as shown in Figures 3.5 and 3.6. Figure 3.5 is the Ford-Walford graph for the VBG model and Figure 3.6 is the graph for Gompertz model. The asymptotic length at an infinitely long period, L∞ was determined for the VBG and Gompertz model as 178 and 126 cm respectively.

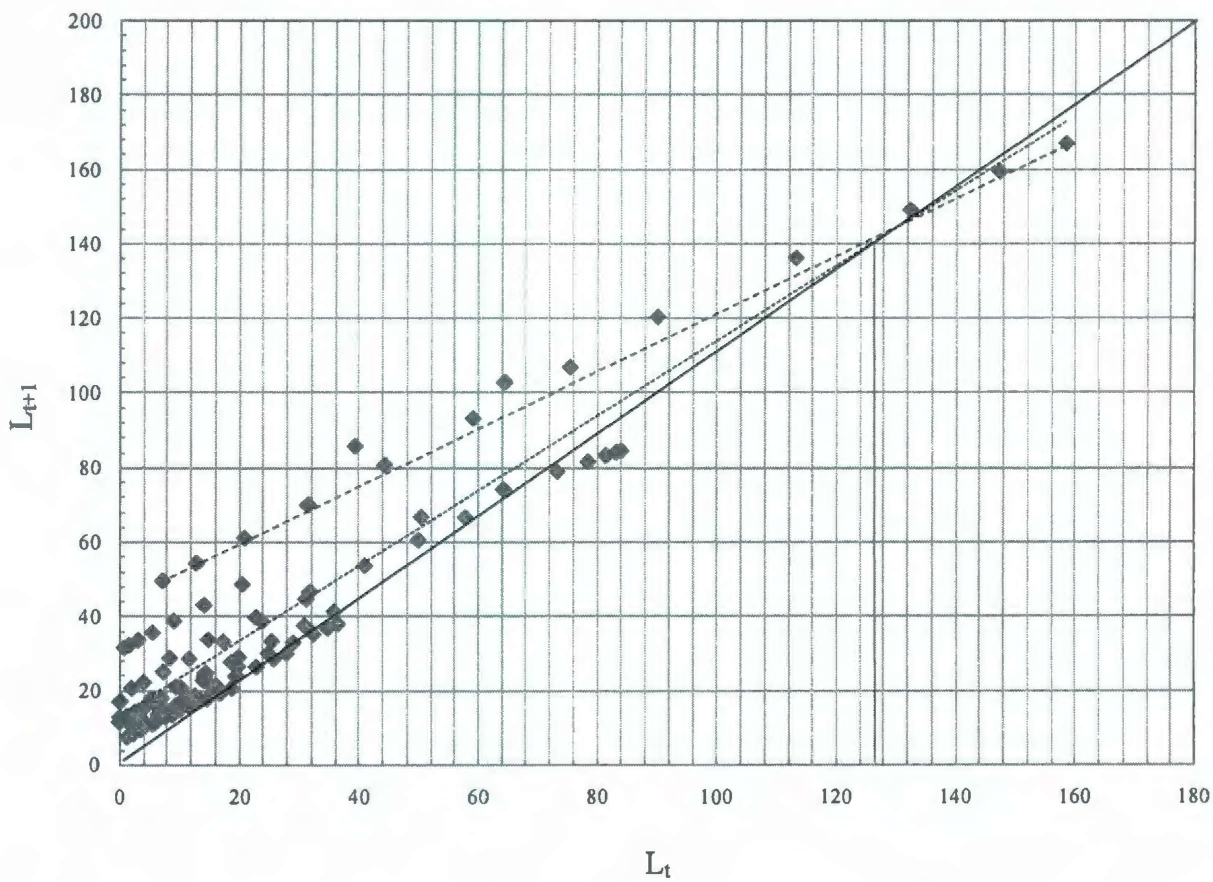

Figure 3.6 Ford-Walford Graphs for the Gompertz Model

(Fishbase, 2008, USDOC, 2007)

Table 3.1 Parameters for Fish Length (after Fishbase, 2008 and USDOC, 2007)

Species	Parameters		L_{max} (cm)	$L\infty$ (cm)	k (1/yr)	t_0 (yr)
	a	b				
Red mullet	0.005	3.23	30	24.62	0.329	-0.329
Gilthead seabream	0.03	2.67	70	58.60	0.263	-0.787
Common pandora	0.017	2.85	60	35.42	0.196	-1.17
European hake	0.004	3.13	140	71.60	0.182	-0.736
Atlantic horse mackerel	0.007	2.98	70	40.83	0.227	-0.865
Mediterranean horse mackerel	0.007	3.01	60	34.31	0.344	-0.743
Atlantic mackerel	0.002	3.37	60	40.34	0.39	-1.288
Pacific cod	0.0079	3.097	119	94.57	0.266	-0.660
Atlantic cod	0.0104	3.00	200	106.03	0.195	-0.345
Pacific halibut	0.0031	3.24	258	182.1	0.065	-0.675
Atlantic Halibut	0.0195	3.00	470	218.13	0.08	-0.210
Swordfish	0.0078	3.21	455	272.73	0.173	-1.694
Skipjack tuna	0.0678	3.29	110	85.01	0.629	-0.767
Yellowfin tuna	0.0214	2.974	239	185.17	0.382	-0.378
Southern bluefin tuna	0.0167	3.06	245	228.60	0.144	-0.35
Halibut	0.0031	3.24	258	187.00	0.07	-1.11

The fish species shown in Table 3.1 are common in Canada and especially in Atlantic Canadian region.

To determine the curvature parameters k and condition parameter t_0 two Equations were developed from Table 3.1 in terms of the asymptotic length L_∞. The two Equations are:

$$k = C_1 \times \exp(C_2 \times L_\alpha) \qquad (3.7)$$

$$t_0 = C_3 + C_4 \times L_\alpha \qquad (3.8)$$

Where,

k=Curvature parameter

t_o=Condition parameter

L_∞=Asymptotic length of the fish

C_1, C_2, C_3, C_4= Equation co-efficients, which are, C_1=0.437, C_2=-0.0089, C_3=-0.9434 and C_4=0.0029.

The co-efficients were estimated by using the statistical software Minitab, DataFit and MS-Excel, and a R^2 values for k and t_0 were 0.88 and 0.93 respectively.

3.4 Fish Length-Weight Model

Numerous articles are available in research journals dealing with the length-weight relationship in fisheries, (Ricciardi et al., 1995). The inherent relationship between length and weight of a fish is usually described by the nonlinear allometric model, where the ratio of body depth to length varies as:

$$W = aL^{b} \qquad (3.9)$$

where,

W = weight of the fish at a particular age

a = growth parameter for a particular fish

b = slope of the growth-length curve

L = length of the fish at a particular age

Parameters a and b usually can be estimated by the method of least squares (Prajneshu and Venugopalan, 1999). The goodness of fit can be assessed by R^2 values.

Most of the length-weight models have been generated from Equation 3.9. The parameters a and b can vary in the range of 0.002 to 0.678 and 2.67 to 3.24 respectively as shown in Table 3.1.

Table 3.2 Fish Length-Weight Parameters (Morato, et. al., 2001; Cherif et al., 2008)

No. of Species	a	b	No. of Species	a	b
664	0.004	3.28	44	0.002	3.35
1099	0.007	3.12	55	0.006	3.18
1763	0.005	3.23	99	0.002	3.37
124	0.052	2.8	89	0.0344	2.813
271	0.014	2.72	32	0.0064	3.444
395	0.03	2.67	16	0.0081	3.445
183	0.033	2.72	511	0.0082	3.446
287	0.01	2.86	136	0.0104	3.447
470	0.012	2.9	65	0.0141	3.448
285	0.01	2.84	147	0.0142	3.449
613	0.018	2.84	77	0.0461	3.45
898	0.017	2.85	31	0.0229	3.451
121	0.03	2.82	421	0.0058	3.452
209	0.012	2.94	129	0.0049	3.453
330	0.014	2.87	244	0.0087	3.454
187	0.004	3.17	1178	0.0111	3.455
340	0.005	3.11	231	0.018	3.456
527	0.004	3.13	446	0.0166	3.457
71	0.003	3.01	49	0.0084	3.458
172	0.009	2.98	124	0.0052	3.459
243	0.007	3.06	15	0.0169	3.46
85	0.007	3	95	0.0049	3.461
144	0.007	2.98	355	0.0141	3.462
229	0.007	2.98	28	0.0197	3.463
182	0.007	2.99	306	0.0126	3.464
280	0.009	2.9	1149	0.0069	3.465
462	0.007	3.01	90	0.0125	3.466
28	0.005	2.92	374	0.0097	3.467
89	0.01	2.98	42	0.0069	3.468
117	0.009	2.84	58	0.0091	3.469

To determine the length-weight model length-weight parameters, fish population data were collected from different literature sources combining 17,504 fish species of male and female sex (Cherif et al., 2008; Morato, et. al., 2001) as shown in Table 3.2. The parameter values were fitted to determine the length-weight model by using statistical analysis. The values of *a* and *b* were determined from weighted average.

The length-weight models were developed from Table 3.2 as follows, with the value of parameter a=0.012247 and b=3.185 with a R^2 value of 0.91.

$$W = 0.012247 \quad L_t^{3.185} \qquad (3.10)$$

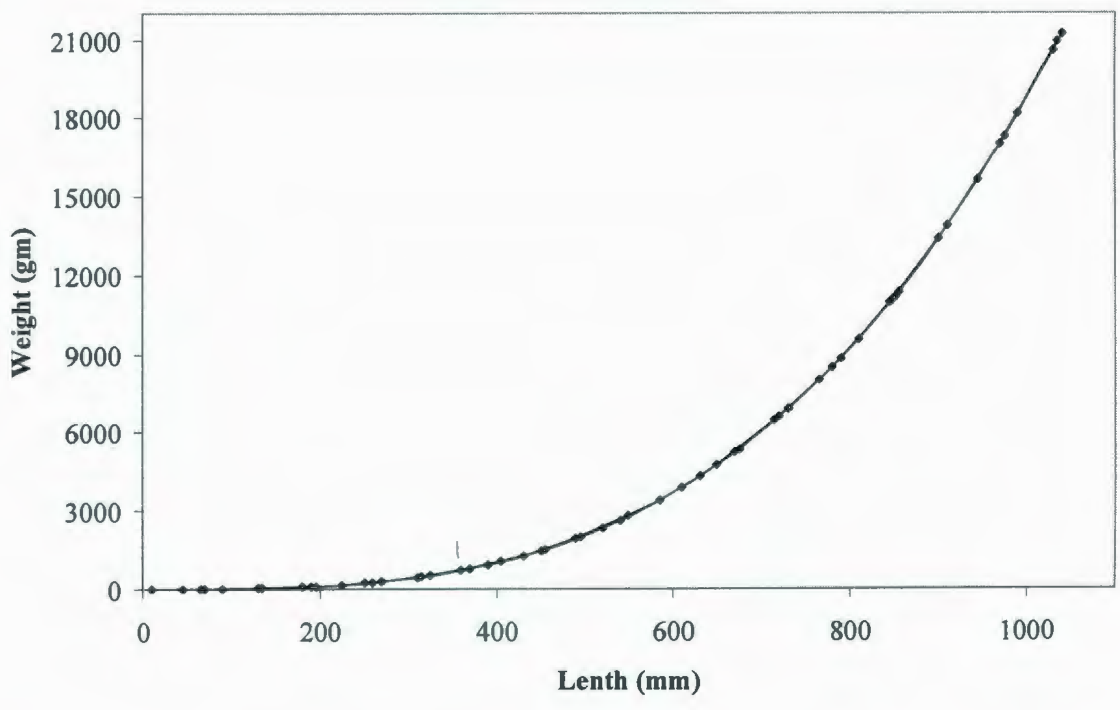

Figure 3.7 Fish Length-Weight Relationships (Morato, et. al, 2001; Cherif et al., 2008)

For this study we considered the length-weight prediction for Cod, Mackerel and Halibut. Comparison of length data was conducted by using the VBGM (Equation 3.2) and the Gompertz (Equation 3.6) model and then weight was calculated by using Equation 3.10.

The Atlantic Cod (*Gadus morhua*) which is a very popular commercial fish in Atlantic Canada was considered in the main length-weight calculation. In the warm southern end of the Canadian range, Cod attain maturity at 2 to 3 years of age. In the cold region of Northeast Newfoundland shelf they mature at between 5 to 7 years of age (COSEWIC, 2003). At two years of age the weight of 3050 Atlantic Cod varied from 677 to 1209 gm (Rosenlund and Skretting, 2006). By using the Equations and statistical values discussed above the length of fish and weight at different ages can be compared. The data estimation for Atlantic Cod was justified with the published data as shown in Figure 3.8.

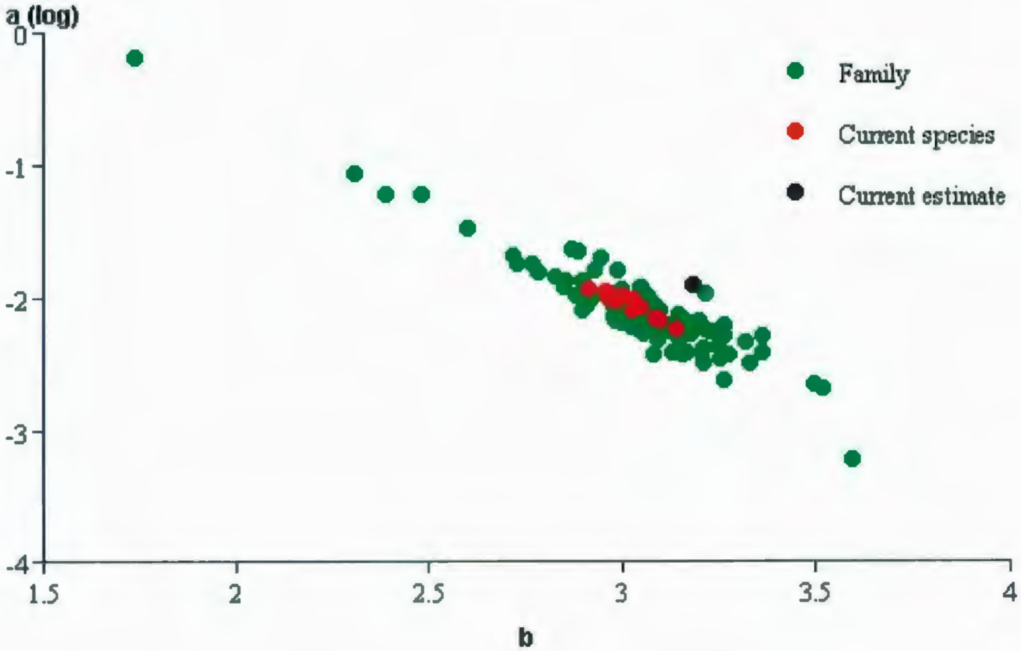

Figure 3.8 Comparison of Proposed Model with Existing Data for Atlantic Cod (Fishbase, 2008)

The study model data comparison for Atlantic Cod with the published data by Hunt (1996) showed that, the VBGM model provided more realistic estimation of length-weight parameters. As shown in Figure 3.9 the VBGM is in better agreement with the studied data then the Gompertz model.

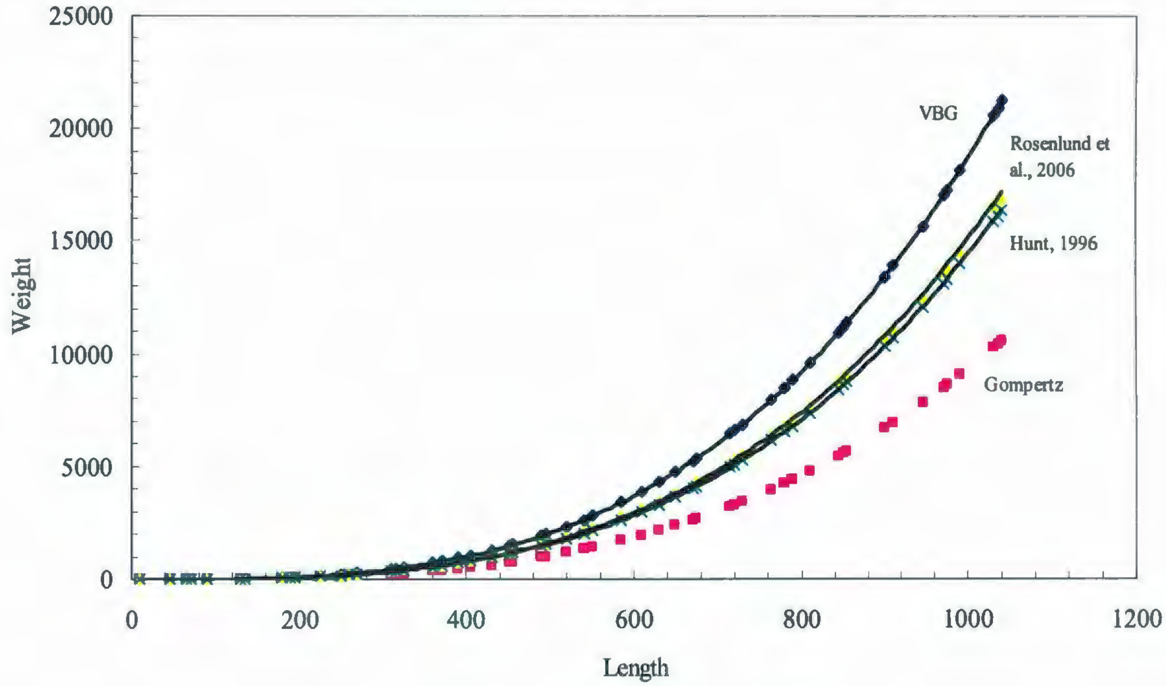

Figure 3.9 Comparisons of Fish Growth Models
(Hunt, 1996; Rosenlund and Skretting 2006)

3.5 Contaminants in Fish

The concentrations of pollutants in the fish tissue need to be determined in order to assess the risk. From a literature review the concentrations of pollutants at the discharge point, C_0 can be estimated. The dilution of the pollutant then can be estimated by applying the dilution model available for produced water. By using the US EPA (2000) recommendation, the contaminants concentrations in fish tissue can then be calculated.

Exposure concentration in fish can be calculated by using the diluted concentrations of pollutants. After the discharge of the produced water into the ocean it mixed with the ambient water and became diluted. The discharge velocity is much higher than the ambient seawater velocity and the point of discharge is located at sufficient depth below the water surface to enhance dilution (Mukhtasor, 2001). As stated by Furulolt (1996), the typical initial dilution in the North Sea is 1000 fold within 50 to 100 m of the discharge. To estimate the concentrations of the produced water contaminants and chemicals, hydrodynamic modeling is important and there are various models available to estimate the dilution for produced water (Mukhtasor 2001, Niu 2008). A simple dilution model can be described as (Ray and Engelhardt, 1992),

$$Dilution = \frac{V \times D \times W}{Q_e} \qquad (3.11)$$

Where,

V= Ambient flow velocity

D= Water depth

w= Width of zone of dilution

Q_e= Effluent flow

Figure 3.10 represent the horizontal flow profile for the Equation 3.11 dilution model.

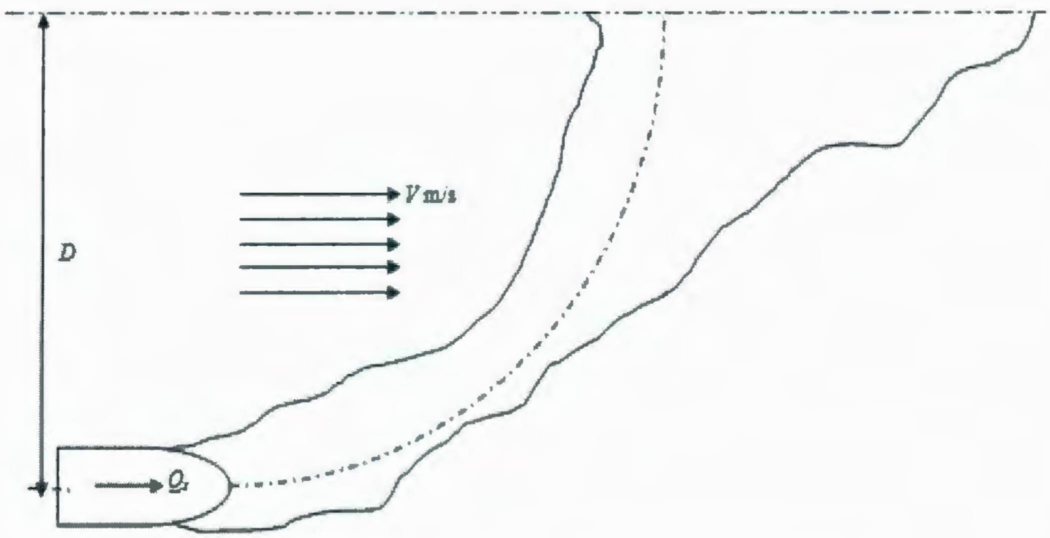

Figure 3.10 Flow Profile for General Dilution Model

Ambient flow velocity depends on weather conditions and the depth of water. In the Gulf of Mexico the surface currents vary from 0 to 30 cm/sec with bottom currents of 3 cm/sec (Ray and Engelhardt, 1992). Generally for offshore oil and gas platforms the ambient flow varies from 0.03 to 0.3 m/s (Somerville et al., 1987).

Depth of water is also another variable parameter and is considered to be shallow water depth for offshore platforms (US EPA, 1991). It can vary from 2.5 m to 150 m depending on the locations and type of the platforms (Meinhold et al., 1996; Brandsma and Smith, 1996). For zone of dilution the usual selection range varies from 100 to 500m (Ray and Engelhardt, 1992). The effluent discharge rate ranges from 3.68×10^{-6} to 0.276 m^3/sec (US EPA, 1993). Another study shows the average discharge varies from 3.31×10^{-4} to 0.289 m^3/sec (Walk, Haydel & Associates, 1984).

However with complex seawater conditions several other dilution models are proposed to incorporate the real time situations. The dilution model by Lee and Cheung (1991), Lee and Neville-Jones (1987), Proni et al. (1994), Huang et al. (1998) and Mukhtasor (2001) are some of the common dilution models for produced water discharges. The Chemical Hazard Assessment and Risk Management (CHARM) model was developed to evaluate the potential environmental risks posed by chemicals used offshore (Stagg et al., 1996).

Within the scope of this study, the dilution model by Rye et al. (1996) was used which is as follows,

$$\frac{C_o}{C_{\exp}} = \frac{v}{Q}\sqrt{96K_z\frac{x^3}{u}} \qquad (3.12)$$

Where,

C_o= Concentration of pollutant at the discharge point (μg/l),

C_{exp}= Exposure concentration for fish (μg/l),

v= Horizontal diffusion velocity (m/s),

K_Z= Vertical diffusion coefficient (m^2/s),

Q= Effluent discharge rate (m^3/s),

x= Horizontal length of consideration (m),

u=ambient current velocity (m/s).

The current speed was assumed to follow a lognormal distribution of (-3.29, 0.96) (Mukhtasor, 2001). For these conditions, the V *and* K_z values were assumed to be 0.013 m/s and 0.01 m^2/s, respectively (Rye et al., 1996). The influence zone was assumed here as the minimum initial near field dilution model of 100 m from the point of discharge (Mukhtasor, 2001). For conservative analysis the effluent discharge rate was considered to be 0.212 m^3/s as discussed earlier (on Page 54).

Amount of total contaminants in fish can then be calculated as,

$$C_L = C_{\exp} \times BCF \times BAF \qquad (3.13)$$

Where,

C_L= Concentration of contaminant in lipids of a fish (μg/kg)

C_{exp}= Exposure concentration for fish

BAF= Bio-available factor

BCF= Bio-concentration factor

During the bioaccumulation of PAHs, PAHs are desorbeds or are released into a solution from the solid medium and then partition into the lipid-rich tissues of the marine organisms. For that reason, the bioavailability of PAHs from sediments and food is less than that from the solution in water (Neff, 2002). Swapan et al. (2004) reported the distribution of naphthalene and fluoranthene in 11 fish species from Hiroshima Bay, Japan. The mean values for Naphthalene varied from 4.54 to 20.50 μg/g and for Fluoranthene from 0.44 to 6.70 μg/g. BCF values of 224 to 490 were reported among bluegill sunfish (McCarthy and Jimenez 1985, Spacie et al., 1983) and 480 among Golden Ide exposed to benzo(a)pyrene (Freitag et al. 1985). Northern pike exposed for 10 or 21 days to benzo(a)pyrene in water produced a *BCF* ranging from 50 to 80000 in internal organs, with the greatest bioconcentration occurring in the gallbladder and bile (Balk et al., 1984). A *BCF* of 920 was reported in rainbow trout (Gerhart and Carlson, 1978). Neff (2002) estimated the equilibrium *BCF* for marine fish tissues which showed higher values for naphthalene and its homologous compounds ranging from 170 to 3550. For phenanthrenand its homologous compounds the value rangeed from 1620 to 3360. However, these estimated *BCF*s are for long-term exposure and may not be attained in a natural field situation. The lognormal distribution of the *BCF* value is determined as (16.145, 72.682).

The total amount of contaminants accumulated in the fish can be calculated by using the weight of fish as,

$$W_C = C_L \times W_t \times F_L \tag{3.14}$$

Where,

W_c=total accumulated contaminants in fish (μg),

C_L= concentration of contaminants in lipid of a fish (μg/kg),

W_f=Weight of fish (kg),

F_L=Fraction of lipid concentration in fish

The weight of fish, W_t can be determined by using the fish length-age and age-weight model. The Storage and Retrieval (STORET) database (STORET, 2007) provided the percent lipid content in different marine fish such as halibut, herring, mackerel, salmon, and sea trout. The National Study of Chemical Residues in Fish (NSCRF) collected data from over 119 different species representing 33 taxonomic families (NSCRF, 2007), which includes common marine fish such as Atlantic Cod. Specific data on marine fishes available in the offshore oil production area is not available and in the absence of particular site specific information, data from these two prominent databases were used. The STORET database shows that mean fillet percent lipid varies between 0.8 and 4.5, and the mean whole body percent lipid ranges from 3.8 to 6.3 for various groups of fish species, whereas in NSCRF these values range from 1.6 to 4.9 and 3.8 to 6.3 percent, respectively. This data shows a lognormal distribution of (1.139, 1.032).

The US EPA recommends to calculate the fish tissue concentrations in edible part of fish only.

$$C_f = \frac{W_c}{F_{epr} \times W_t} \qquad (3.15)$$

Where,

C_f=concentration in fish tissue (μg/kg),

F_{epr}=ratio between the weight of edible part to the weight of whole fish

W_c=total accumulated contaminants in fish (μg),

W_t=Weight of fish (kg),

The edible data for fish can be calculated as the sum of the moisture and lipid content in a fish. According to US EPA (1996) this value ranges between 64-87% with a mean value of 78% which results in a lognormal distribution of (4.36, 0.063). The variation of moisture and lipid content in different fish species are tabulated in Table 3.3.

Table 3.3 Moisture and Lipid Contents of the Selected Species

Species	M/C (g/100g)	Total Lipid (g/100g)	Form	Reference
Cod	81.90	0.74	Fillet	Shahidi and Dunajski, 1994
Halibut, Atlantic; Pacific	77.92	1.812	Raw	US EPA, 1996
Halibut, Greenland	70.27	12.164	Raw	
Haddock	79.92	0.489	Raw	
Herring, Atlantic	72.05	7.909	Raw	
Herring, Pacific	71.52	12.552	Raw	
Salmon, Alaska	66	11.7	Raw	
Salmon, Atlantic	68.9	10.8	Raw	
Salmon, Atlantic Wild	68.5	6.34	Raw	
Salmon, Pink	76.4	3.45	Raw	
Salmon, Pink	70.5	4.83	Canned	Jacob, E., 2007
Salmon, Red	70.2	8.56	Raw	
Salmon, Red	67.5	7.31	Canned	
Tuna	65.17	8.57	Raw	Morrissey, 2003
Shrimp	52.86	10.984	Cooked	US EPA, 1996
Lobster, mixed species	72.56	1.421	Canned	US EPA, 1996

3.6 Risks in Human Health

Human populations can be exposed to the produced water contaminants by direct contact (offshore oil and gas workers) or through seafood ingestion. The effect of direct contact is negligible and several safety measures are in place for that. The uptake of contaminants through oral ingestion is considered in this study. The exposure pathway is shown in Figure 3.11.

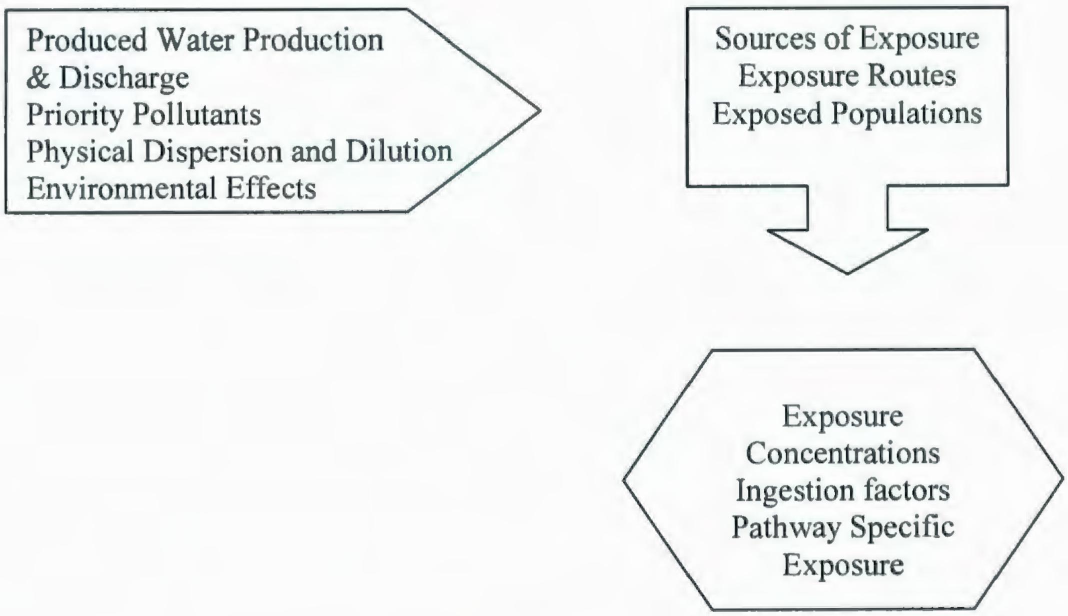

Figure 3.11 Exposure Assessments from Produced Water

Many variables contribute to the range of contaminant levels ingested with fish tissue, including the size and type of fish, the cooking preparation, and the cooking methods. Because these site-specific and cooking-specific variables are most often unknown in a risk assessment situation, conservative assumptions were taken for this study by assuming that, there is no loss of contaminant due to the cooking method.

According to the US EPA (1998) the daily intake of any contaminants through oral ingestion can be calculated as,

$$I = \frac{C_f \times FIR \times EF \times ED}{BW \times AT} \quad (3.16)$$

For PAH intake Equation 3.16 can be modified as,

$$I = \frac{C_f \times FIR \times EF \times ED \times Fr \times 10^{-6}}{BW \times AT} \quad (3.17)$$

Where,

I = total PAHs intake, the amount of chemical at the exchange boundary in mg/kg body weight/day,

C_f = the concentration of contaminants in fish tissue, calculated from Equation 3.15

FIR= daily fish ingestion rate (g/day),

EF= exposure frequency (days/yr),

ED= exposure duration (yr),

BW= body weight (kg),

AT= averaging time (days),

Fr= fraction of ingested fish, and

10^{-6}=conversion factor for μg/kg.

The parameters used in this study are described in the following sections.

3.6.1 Fish Ingestion Rate (*FIR*)

The amount of fish that people eat is referred to as ingestion rate or consumption rate. The US EPA 95th percentile value of fish intake is 132 g/day (US EPA 1991). The upper 95th percentile fish ingestion rate of 170 g/day was recommended for Native American Subsistence Populations by the US EPA (1996). For human health risk assessment the US EPA (1999) used the 99th percentile fish consumption rate of 177g/day. The use of a lognormal distribution was suggested by the US EPA (1996) for long-term human health risk assessment. Meinhold et al. (1996) derived a lognormal (3.455, 0.622) distribution for fish caught near an open bay platform in Louisiana. For Atlantic Canada, there is no available fish ingestion rate for marine fishes. In order to capture the more realistic local conditions a questionnaire survey was conducted in the St. John's, NL area. The data shows a lognormal distribution of (0.45657, 4.1748) as shown in Table 3.4. The detail of this survey is discussed in section 3.7.

Table 3.4 Fish Ingestion Rate (from survey data, as discussed in Section 3.7)

	Intake (gm/day)
Arithmetic Mean	73.54
Median	128.56
Standard Deviation	44.18
Minimum	42.86
Maximum	214.29
95th Percentile	214.29

3.6.2 Exposure Frequency (*EF*)

The number of occurrences in a given time frame (usually in lifetime) of contact of a stressor with a receptor is known as exposure frequency. The US EPA (1991) recommended a minimum 2 weeks per year absence from the exposure. According to this recommendation, the exposure period for all exposure pathways has been assumed as 350 days per year. This will provide a conservative estimation of risk.

3.6.3 Exposure Duration (*ED*)

Exposure duration is the length of the time for which exposure to certain stressors occurs through a specific pathway. For many instances the exposure duration may continue long after the exposure contact. For more realistic exposure duration, the total number of years a person is likely to reside in the vicinity of the pollutant are calculated. The US EPA Office of Solid Waste recommends the exposure duration for subsistence fisheries and adult residents of 30 years (US EPA, 1998).

3.6.4 Body Weight (*BW*)

Body weight can be varying over the age and sex of population. For risk estimation, US EPA suggested to consider two age groups: adult and child. According to US EPA (1999), the body weight for adult receptors was 70kg. For this study, only the adult population was considered. The survey results as mentioned in section 3.7 show an average adult body weight as 81.22 kg with a lognormal distribution of (0.7321,4.9466).

3.6.5 Averaging Time (*AT*)

The averaging time is the period over which exposure is averaged for carcinogenic effects. Human life expectancy can vary in different regions of the world as shown in Table 3.5. For this study the averaging time was considered to be 70 years, according to US EPA (1999) for carcinogenic risk. For non-carcinogenic hazard, the averaging time is the same as the exposure duration.

Table 3.5 Life Expectancy in Different Regions of the World

Region/Country	Life Expectancy (years)
Australia	79
Canada	79.2
France	78.7
Japan	81.3
UK	77.9
USA	76.9
World	66.7

3.6.6 Fraction of Contaminated Fish Ingested (*Fr*)

Throughout the exposure period, it is unrealistic to assume that all the fish ingested are from the contaminated site. The US EPA study shows that for the 1-20 age group, 0.123 kg/day of recreational fish was consumed out of a total of 0.219 kg/day ingestion. On the basis of the data provided by the US EPA (1997) and Dellenbarger et al. (1993), marine fish were almost 50% of the total fish ingestion. Also as all the marine fish need not necessarily come from the contaminated zone, an assumption of 50% of the total ingested fish from the contaminated zone provide a conservative estimates.

3.7 The Questionnaires Survey

For the Atlantic Canada region, there was no reported study for the marine fish consumption. The US EPA recommends that fish ingestion rate and exposure frequencies are very generic and can vary from region to region. To get more realistic information, a fish consumption survey was conducted. The survey was conducted online by using the popular online survey tool: Zoomerang (2009). This survey tool is widely used in different research studies and collects the data ensuring anonymity of the survey respondents (Shirley et al., 2007). By using this tool a set of questions and answers options were prepared (details in Appendix). The survey link was then published and advertised among the people of St. John's, NL and its vicinity through the graduate students e-mail list of MUN, engineering e-mail list of MUN, local Facebook groups of St. John's, NL and different local e-mail lists. The focus groups of the survey were students, professionals, international demographic groups and other local groups. It was assumed that these groups well present the communities of an Atlantic Canadian region. The survey was conducted for three weeks.

In total 62 respondents completed the survey reporting information over 215 people in different households and family sizes. 28% of respondents were members of ethnic groups or non-Canadians, 61% were Canadian and 11% did not disclose their ethnicity.

95% of the responders indicated they consumed sea fish. The types of fish consumed are shown in Figure 3.12.

Figure 3.12 Types of Fish Consumed in Atlantic Canada

Among the others category, the survey showed most of the people mentioned freshwater fish, such as, Tilapia, Catfish, Trout, Rainbow trout, Crab, Lobster, Caplin, Mussels, Scallops, Haddock, Pollock, Alaskan Pollack, Sole, Herring, Mackerel etc.

The Majority of the people preferred fish fillets as shown in Figure 3.13. The survey showed that some people also ate cod tongues and cheeks, steak and canned fish.

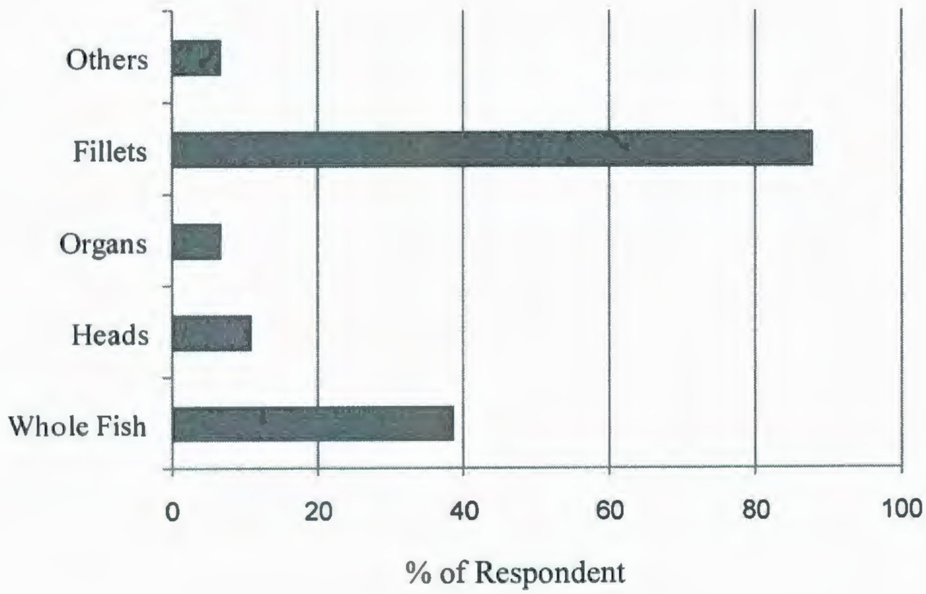

Figure 3.13 Portion of Fish Ingested (%)

The choice of cooking is an important factor for fish consumptions. Frying and bake are the two most popular ways of cooking according to the survey results. Broiling, soup, raw stew, bbq, steamed and other cooking methods were also popular. Figure 3.14 summarizes the details of fish cooking.

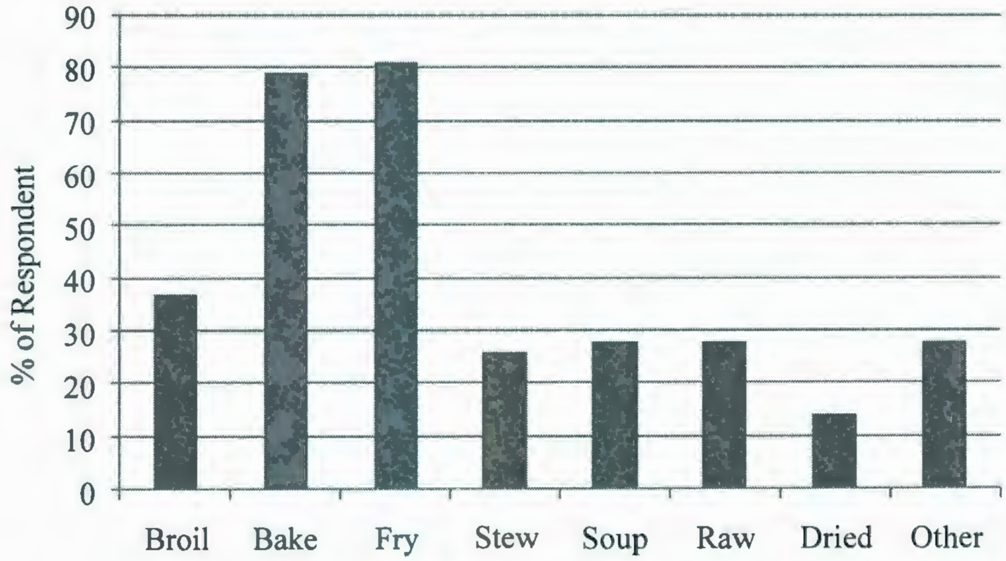

Figure 3.14 Different ways of Cooking Fish

In the study area, 40% of the respondents ate fish less than once a week and 45% ate fish 1-2 times a week. Only 2% reported to eat fish daily; whereas 13% mentioned that they ate fish 3-5 times a week. Figure 3.15 shows the frequency of fish intake in the area

There are several other questions regarding the fish ingestion and awareness regarding possible health risk. The results will be discussed in relevant sections.

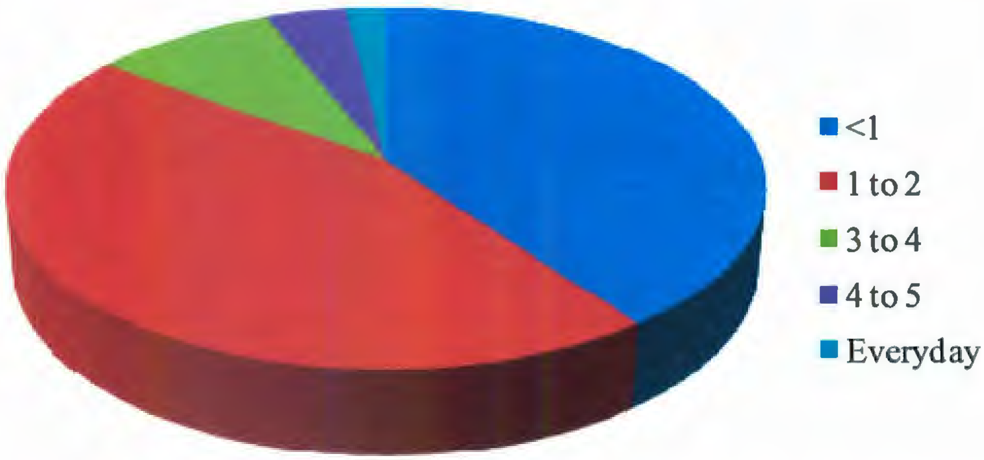

Figure 3.15 Frequency of Fish Purchase per Week

3.8 Characterization of Human Health Risk

Once the daily intake of the contaminants is determined, the risk value can be estimated. The exposure pathways for cancer risk (upper-bound excess lifetime cancer risks) and non-carcinogenic hazards can be assessed for oral intake. As more than one pollutant was considered, the total effect was calculated by combining the individual estimations.

3.8.1 Risk Characterization for Non-Carcinogens

For non-carcinogens, a threshold value is considered up to which level there is no adverse effect and it is determined as,

$$HQ = \frac{I}{R_f D} \qquad (3.18)$$

Where,

HQ= Hazard quotient (unit less)

I= Chronic daily intake (mg/day; from Equation 3.17)

$R_f D$= Reference dose of the pollutant chemicals (mg/kg-day)

According to US EPA, the HQ values less than 1 indicates that the hazard value is within the acceptable limit. The hazard index can be calculated for the group of pollutants by adding the individual hazards in the same exposure pathway as,

$$HI = \sum_i HQ_i \qquad (3.19)$$

Where,

HI= Total hazard for a specific pathway

HQ_i= Hazard quotient for contaminant i

By considering individual HQs additive in nature, the HI can be determined by using the probabilistic summation approach as, For i-no of chemical contaminants, the summation approach can be can be implemented as,

$$R^{2}_{R/HI} = R(1) + R(2) - R(1) \times R(2)$$

$$R^{3}_{R/HI} = R(1+2) + R(3) - R(1+2) \times R(3)$$

$$R^{4}_{R/HI} = R(1+2+3) + R(4) - R(1+2+3) \times R(4)$$

$$R^{5}_{R/HI} = R(1+2+3+4) + R(5) - R(1+2+3+4) \times R(5)$$

....

$$R^{i}_{R/HI} = R(1+2+\ldots\ldots + R_{i-1}) + R(i) - R(1+2+\ldots + R_{i-1}) \times R(i) \quad (3.20)$$

Where,

1,2…. to *i…..* is the number of pollutants respectively

R refers to risk or hazard quotient accordingly

The reported available quotient values of priority PAHs are given in Table 3.6. In the absence of available data for other PAH compounds surrogate data from Pyrene can be taken as R_fD values of Benz(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-c,d)pyrene and Dibenz(a,h)anthracene (DWQ, 2008).

Table 3.6 Available Hazard Quotients for PAHs (after Monteduro et al., 2007)

PAH Compound	R_fD (mg/kg-day)
Naphthalene	0.02
Pyrene	0.03
Acenaphthene	0.06
Fluoranthene	0.04
Fkuorene	0.04

3.8.2 Risk Characterization for Carcinogens

Risk assessment for carcinogens represents the incremental probability that an individual will develop cancer over a lifetime as a result of exposure to a carcinogenic pollutant. The cancer risk can be estimated as,

$$R = I \times SF \qquad (3.21)$$

Where,

R= Cancer risk

I= Chronic daily intake (from Equation 3.17)

SF= Cancer slope factor $(mg/kg\text{-}day)^{-1}$

Toxicity data for a majority of the parent PAH compounds and the substituted parent compounds are limited. In performing the risk assessment, either the PAHs with insufficient toxicity data are neglected or an estimate of toxicity is used. The US EPA provided relative potency factors (RPFs) to evaluate the cancer potency. Toxic equivalency factors (TEFs) provided by the Risk Assessment Information System (RAIS) are toxicity estimates derived relative to the activity of a reference compound, normally the most toxic of a specific family of compounds. RAIS values can be used for both cancer and non-cancer risk estimation. For this estimation, the slope factor of benzo(a)pyrene is taken as a standard, and for other PAH compounds, slope factors were determined by considering the structure. Robin et al. (2002) compiled the TEF values from six sources including the RPF values of the US EPA. Table 3.7 shows the cancer slope factors for priority PAHs.

Table 3.7 Available Cancer Slope Factors for PAHs

PAH Compound	CAS No	Slope factor $(mg/kg\text{-}day)^{-1}$
Naphthalene	91203	1.2×10^{-1}
Benz(a)anthracene	56553	7.3×10^{-1}
Chrysene	218019	0.0949
Benzo(b)fluoranthene	205992	0.803
Benzo(k)fluoranthene	207089	0.511
Benzo(a)pyrene	50328	7.3
Indeno(1,2,3-c,d)pyrene	193395	1.825
Dibenz(a,h)anthracene	53703	7.665

Total cancer risk can be calculated as,

$$R_{Total} = \sum_i R_i \qquad (3.22)$$

Where,

R_i= Cancer risk from pollutants i

To calculate the total cancer risk, Equation 3.22 was used by assuming all the pollutants were independent of each other.

3.9 The DISSPROWM Tool

The Decision Support System for Produced Water Management (DISSPROWM) was developed by the Memorial University of Newfoundland in cooperation with the Department of Fisheries and Ocean and SNC-Lavalin. The main objective for developing this tool was to address issues that are critical for the offshore petroleum industries and also to make the tool applicable to industries in their decision-making to manage produced water in a cost effective and environmentally safe manner (Niaz et al., 2009).

The DISSPROWM contains a comprehensive database with information on chemical properties, toxicity and technology, dilution and dispersion models, risk assessment modules as well as information on the best available treatment technology applicable to offshore platforms. The database consists of a SQL Server based database which can handle the user inputs. A schematic of the DISSPROWM database model is shown in Figure 3.16.

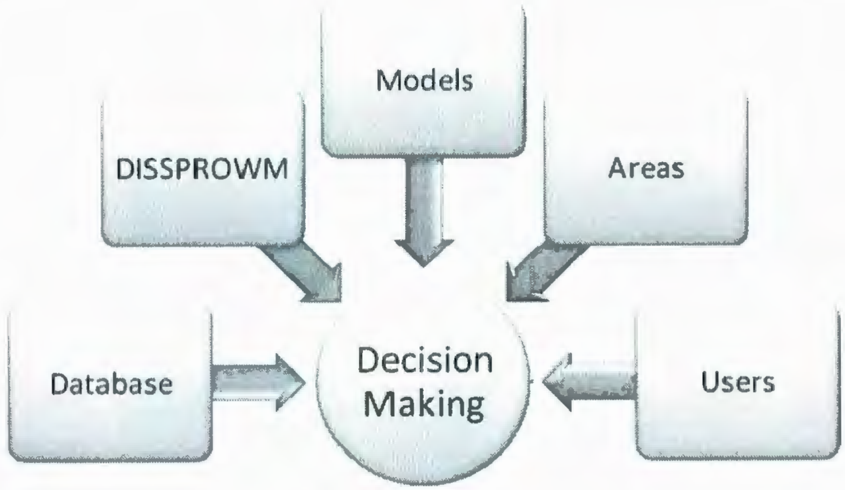

Figure 3.16. The DISSPROWM Database Model

The database contains produced water contaminants, treatment technologies, case studies, costing, and regulatory guidelines. The Graphical User Interface (GUI) of the DISSPROWM is equipped with structured menus and modern toolbar for frequently used functionalities and a context sensitive help system. It has an interactive data entry for produced water contaminants and dispersion model parameters. It has a number of 2D and 3D graphical and tabular display options for displaying prediction of fate and transport of pollutants. It can assess risk and hazard for fish and other marine species as well as human beings from consumption of contaminated fish. From a known concentration of produced water contaminants the system can decide the best available technology (BAT), and its approximate cost. Based on the extent of treatment, it is possible to estimate risk to fish and marine species and human beings and hence a tradeoff between cost and risk can be developed. It takes series of user input in sequence and decides the best available technology and risk to marine habitats and human health.

This tool is a way for decision makers to assess and compare the different scenarios and available options. In this study the tool is used for comparison purpose.

3.10 Summary

The fish growth models suitable for offshore produced water in marine areas were discussed in this chapter. The framework of human health risk assessment was developed based on the US EPA guidelines. The VBGM of fish growth provided more realistic output and was selected for the next step. The variability of concentrations of pollutants in fish tissue, absorption of concentrations in the edible part of the fish tissue, the fish ingestion rate, the body weight were incorporated into the framework. The dilution of produced water was considered by using a simple dilution model. A questionnaire survey was conducted within the local community to get the fish ingestion data and related marine fish information. The data from the survey was incorporated into the model. Other related survey results are discussed in this chapter and in following chapters. A hypothetical case study is presented in the next chapter by using the models discussed in this chapter.

Chapter 4

RISK ASSESSMENT: A CASE STUDY

4.1 Introduction

In this chapter the methodology and concept discussed in Chapter 3 are applied in a hypothetical case study for the Atlantic Canada region. Newfoundland and Labrador are in the developmental phase of their offshore oil and gas industry and exploration continues at a rapid pace; generating millions of dollars in oil revenues and growth in the job sectors. Offshore oil was produced off Canada's east coast from 1992 to 1999 with production from the Cohasset/Panuke Field (COPAN) located 41 km southwest of Sable Island off Nova Scotia, resulting in a total of 44.5 million barrels of light crude (EMPR, 2005). While in 2003 the provincial production contributed approximately 30% of the total Canadian conventional light crude oil production (C-NSOPB, 2008) it is projected to contribute 40% in near future (AIMS, 2009). In 2007 hydrocarbon production from the Newfoundland and Labrador Offshore Area accounted for 42% of Canada's total light crude production with a value of over $10 billion (C-NLOPB, 2008). The oil and gas sector directly contributed 35% of the province's nominal Gross Domestic Product (GDP). The sector represented 27% of total private capital investment in the province, with more than $900 million in capital expenditures in 2007 (C-NLOPB, 2008). The majority of the oil and gas activities are on the Grand Banks, located southeast of Newfoundland on the North American continental shelf. This area consists of a group of underwater plateaus with a relatively shallow depth of 24 to 100 meter depth, where the cold Labrador currents mix with the warm waters of the Gulf Stream. This area is considered one of the richest fishing grounds in the world where Atlantic Cod, Haddock, Capelin, and Shellfish are available. This area also supports large colonies of sea birds such as Northern Gannets, Shearwaters and sea ducks and various sea mammals such as seals, dolphins and whales. The mixing of cold and warm current often causes fog in this area, especially in spring, when the air-sea temperature differences are greatest. Icebergs carried along the edge of the banks by the Labrador currents, are also most numerous in spring. This area is located at 47°06′ N and 55°48′ W as shown in Figure 4.1.

The Grand Banks are one of the richest fishing grounds in the world with ecological varieties of mammals and birds.

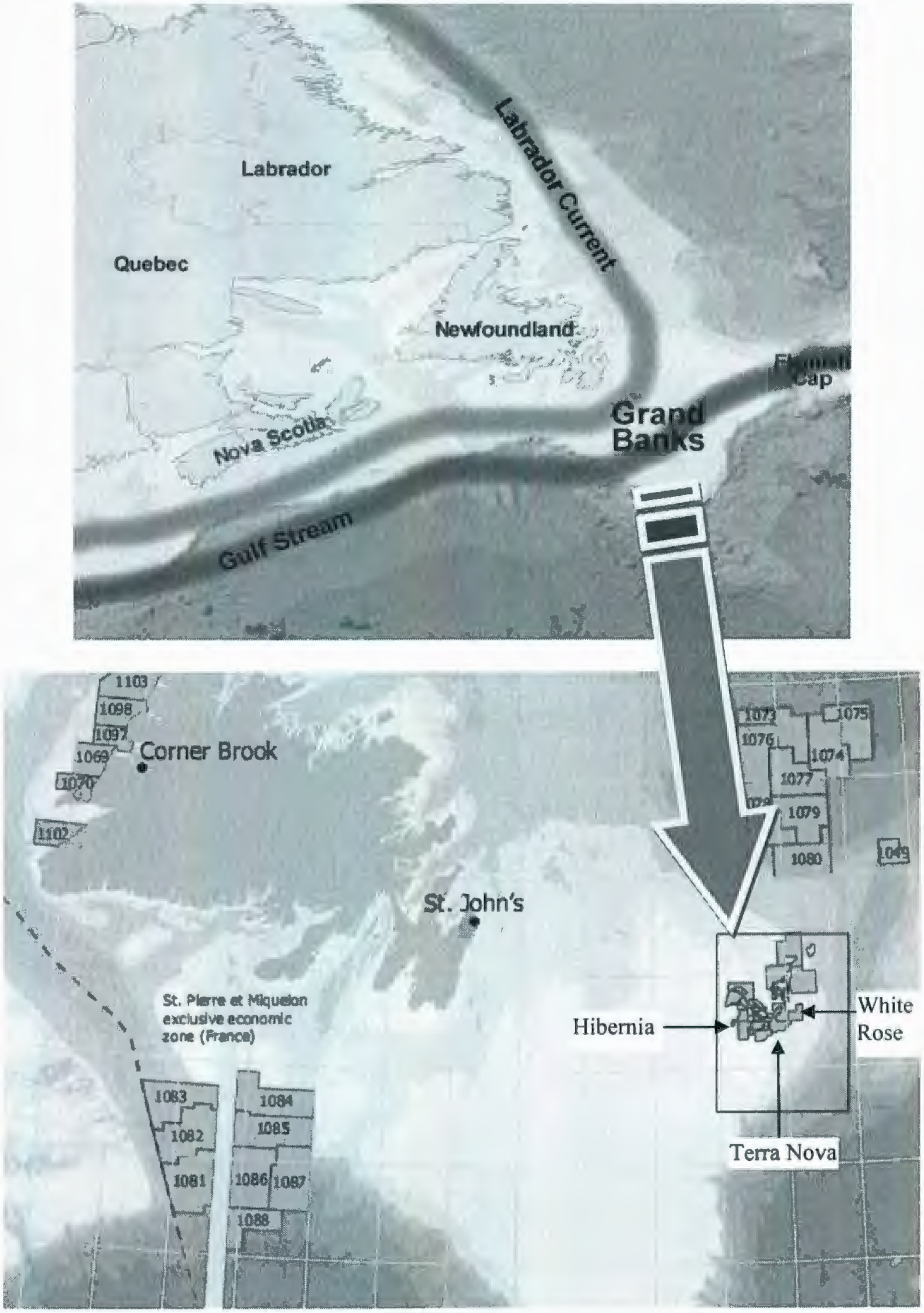

Figure 4.1 Grand Banks (Treeman, 2006, C-NLOPB, 2008)

Overfishing in this area by using modern fishing equipments as well as geopolitical disputes over territorial sea and exclusive economic zone has caused serious decline in fish stocks of the Grand Banks since 1990 and the fishery-based economy of the Newfoundland province has been in a severe crisis. The exploration of oil and gas is greatly contributing to the provincial economical growth.

In Atlantic Canada, five discoveries have been put into production to date. These are: Hibernia, Terra Nova, White Rose, Coheasset and Sable Island. The Cohasset field was operated from 1992 to 1999, producing a total of 7.1×10^6 m^3 of oil. That project is now decommissioned and environmental follow up will be carried on until 2009. Presently three oil fields: Terra Nova, Hibernia and White Rose are in operation. The Hibernia field is located 315 km south-south east of St. John's and began production in 1997. In 2006 the total production of Hibernia, Terra Nova and White Rose was 152 million barrels of crude oil. From the Hibernia South project the Newfoundland province could generate \$10 billion in revenue while Canada could generate \$3.5 billion (BD, 2009). A summary of production of these fields are listed in Table 4.1.

Table 4.1 Grand Banks Petroleum Resources (C-NLOPB, 2009)

	Hibernia	Terra Nova	Hebron	White Rose
Discovered	1979	1984	1981	1984
Oil Reserve (Mbbls)	1244	354	581	305
Oil Produced (Mbbls)	632.88	266.55		122.97
Gas Reserve (Bcuft)	1794	45		3023
NGLs* (Mbbls)	202	3		96
2008-09 Oil Production (Mbbls)	50.8	35.96	Not operated yet	37.17
Average Daily Oil Production (bbls)	139,164	98,517		101,849
2008-09 Gas Production (Bscf)	89.13	59.23		32.81
Produced Water (Mbbls)	45.56	25.86		8.90

Mbbls- thousand barrels; bbls- Barrels

**NGLs-Natural Gas Liquids, it is the petroleum portion of underground reservoir*

The 'reserve' is the volume of hydrocarbons that was proven by drilling, testing and interpreting geological, geophysical and engineering information (C-NLOPB, 2008). The Hibernia field consists of two principal reservoirs: Hibernia and Ben Nevis/Avalon. The field is operated by the Hibernia Management and Development Company (HMDC). The Terra Nova field consists of one reservoir: Jeanne d'Arc and it is operated by Petro-Canada. Reassessment of the reserve is currently ongoing as the production approaches to the previously estimated reserve. White Rose is operated by Husky Energy and also has one principal reservoir: Ben Nevis/Avalon. C-NLOPB (2009) reported that the produced water in the White Rose field is increasing in 2008-09.

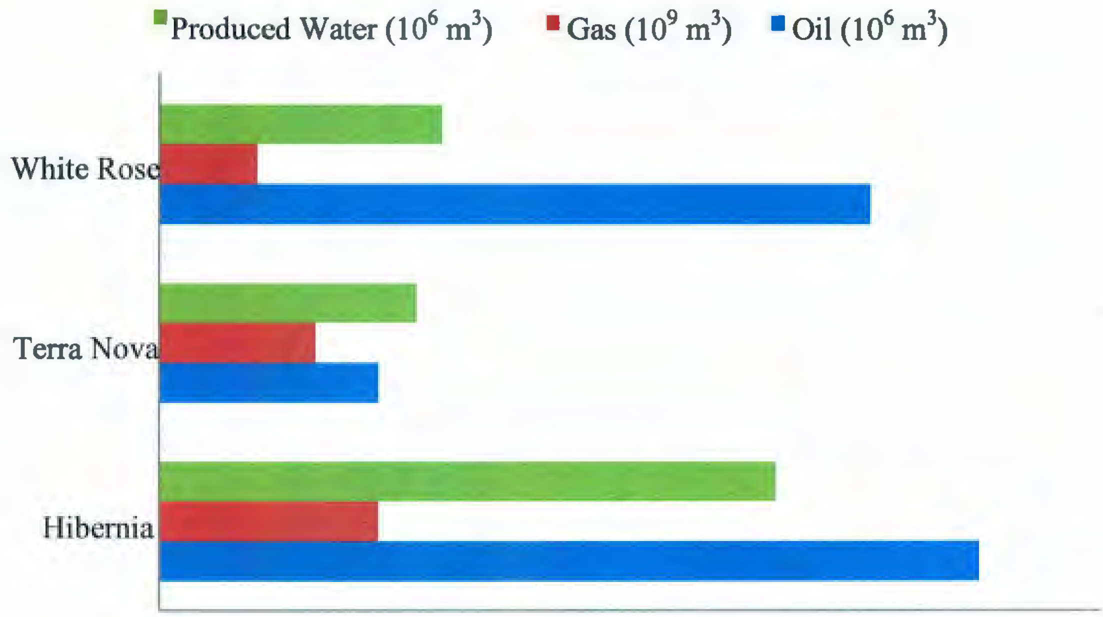

Figure 4.2 Comparison of production: Produced Water, Gas and Oil in Grand Banks

Table 4.2 shows the produced water platform type and treatment methods used in the Grand Banks areas. The Hibernia platform uses the Gravity Based Structure (GBS) platform with the hydrocyclones produced water treatment option. The comparison of productions is shown in Figure 4.2.

Table 4.2 Atlantic Canada Summary (C-NLOPB, 2008; C-NSOPB, 2008)

Field	Produced Water (10^6 m^3)	Platform Type	PW Treatment
Hibernia	5.895	Gravity	Hydrocyclone
Terra Nova	2.445	FPSO	Lack Information
White Rose	2.691	FPSO	Lack Information

FPSO-Floating Production, Storage and Offloading

With the growing activities in this area, the number of reported spills has increased in recent years. In 2007-08 in total 32 spill incidents occurred which included spills of synthetic based mud, crude oil, hydraulic and lubricating oil, diesels and jet fuel and other types of petroleum (C-NLOBP, 2008). From January 1, 2008; the regulatory limit of average discharge was reduced to 30 mg/L from 40 mg/L for oil-in-water in produced water. The amounts of produced water from these sites are shown in Table 4.3.

Table 4.3 Produced Water Discharged in Atlantic Canada (Fred, 2008, Husky Oil, 2000, Fraser et al. 2006)

Field	Maximum Daily Volume (m^3/day)	Average Volume (m^3/day)	Average Oil in Water (mg/L)
Hibernia	24,000	16,996	29.6
Terra Nova	18,300	7,065	25.8
White Rose	30,000	1,010	23.4

4.2 A Hypothetical Case Study

The increasing exploration activities on the East Coast of Canada are creating concerns regarding degradation of the environment and other hazards among researchers and regulatory bodies. This has lead to numerous studies on the environmental and other issues of the oil and gas development in Atlantic Canada (PRAC, 2009; Petro-Canada, 2009).

Chowdhury (2004) and Mukhtasor (2001) developed human health risk and ecological risk methodology using NORMs and a whole effluent approach respectively. In this study human health risks from PAHs of produced water has been developed. Local fish ingestion data were incorporated in the study by using a questionnaire survey and different fish growth models and an ingestion approach were considered for this study.

A hypothetical oil field was considered which is located on the Hibernia, Grand Banks to apply the proposed methodology. The ambient sea water and discharge characteristics of the platform were defined on the basis of C-NLOPB (2008), CAPP (2001), Zhao et al. (2008) and Fraser et al. (2006). A Gravity Base Structure (GBS) was considered with the following characteristics:

- Location: Hibernia, Grand Banks Newfoundland
- Water Depth: 80 m
- Treatment Capacity: 0.212 m^3/s
- Wind Speed: 35 km/hr (mean)
- Air Temperature: 5°C (mean)
- Water Temperature: Varies from -1.7°C to 15.4°C
- Fog: May to July
- Ice/Icebergs: Seasonal floating sea ice, thickness ranging 0.5-1.5 m

The estimated exposure pathway from produced water discharge to human uptake is shown in Figure 4.3. The produced water after treatment is discharged into the sea, where it is diluted. In this dilution zone marine fishes grow and accumulate contaminants in their tissues. These commercial fishes subsequently make their way to the local fish market, supermarket and restaurants.

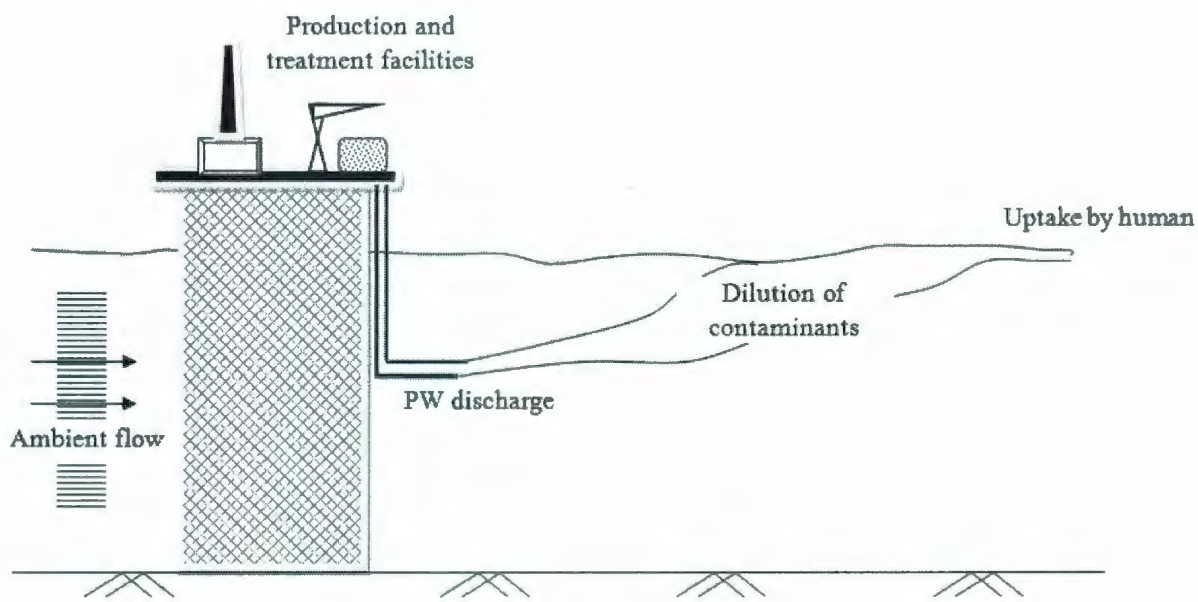

Figure 4.3 Exposure Pathways for Human Uptake

4.3 Estimation of Human Health Risk

The human health risk assessment was done by using the methodology described in Chapter 3 in Sections 3.3 to 3.8.

The fish growth model was developed and discussed in Sections 3.3 and 3.4. The asymptotic length for marine fishes at an infinitely long period, $L\infty$ was determined for the von Bertalanffy growth model (VBGM) and Gompertz model as 178 and 126 cm respectively. The comparison of fish length-weight data with published data indicated that the VBGM represented the length-weight model better than Gompertz model. So for the case study the VBGM was used for the fish tissue concentrations.

The estimate of a daily exposure level of a substance to a human population below which adverse non-cancer health effects are not anticipated is known as the Reference Dose (R_fD) (Le, 2005). Non-cancer hazard assessment can be done for both carcinogenic and non-carcinogenic pollutants. Equations 3.15 to 3.17 have been used to assess the non-cancer hazard risk. Summations of individual hazard risks by using a probabilistic approach provided the hazard index (HI) value.

Many chemicals in produced water are known carcinogens or substances which have the capacity to develop cancer. Depending on their known cancer effects, the US EPA classified different carcinogenic chemicals as carcinogens, probable carcinogens, possible carcinogens, non carcinogens and not classified (US EPA, 1986). With the same intakes calculated by Equation 3.14, the carcinogenic risks were calculated by equations 3.18 and 3.19.

Table 4.4 Input Concentrations of PAH Compounds

PAH Compound	Distribution (μg/l)		
	Lognormal	Triangular	Uniform
Naphthalene & Alkylated Naphthalene	LN (5.77, 1.18)	TN (56, 1211, 3521)	U (-140.94, 3403)
Phenanthrene & Alkylated Phenanthrene	LN (3.24, 1.3)	TN (6.3, 137.60, 400.17)	U (-16.12, 387.42)
Benz(a)anthracene	LN (0.52, 1.26)	TN (0.1, 1.20, 3.41)	U (-0.44, 3.34)
Chrysene	LN (0.36, 1.4)	TN (0.48, 6.37, 18.16)	U (-3.20, 18.88)
Benzo(b)fluoranthene	LN (1.50, 2.03)	TN (0.03, 1.21, 3.4)	U (0.03, 3.4)
Benzo(k)fluoranthene	LN (0.30, 0.29)	TN (0.01, 0.32, 0.93)	U (-0.17, 0.87)
Benzo(a)pyrene	LN (0.66, 0.70)	TN (0.20, 0.64, 1.10)	U (0.20, 1.10)
Indeno(1,2,3-c,d)pyrene	LN (3.09, 2.19)	TN (0.01, 0.20, 0.40)	U (0.01, 0.40)
Dibenz(a,h)anthracene	LN (2.60, 2.741	TN (0.01, 0.59, 1.20)	U (0.01, 1.20)

LN: Lognormal distribution; TN: Triangular distribution; U: Uniform distribution

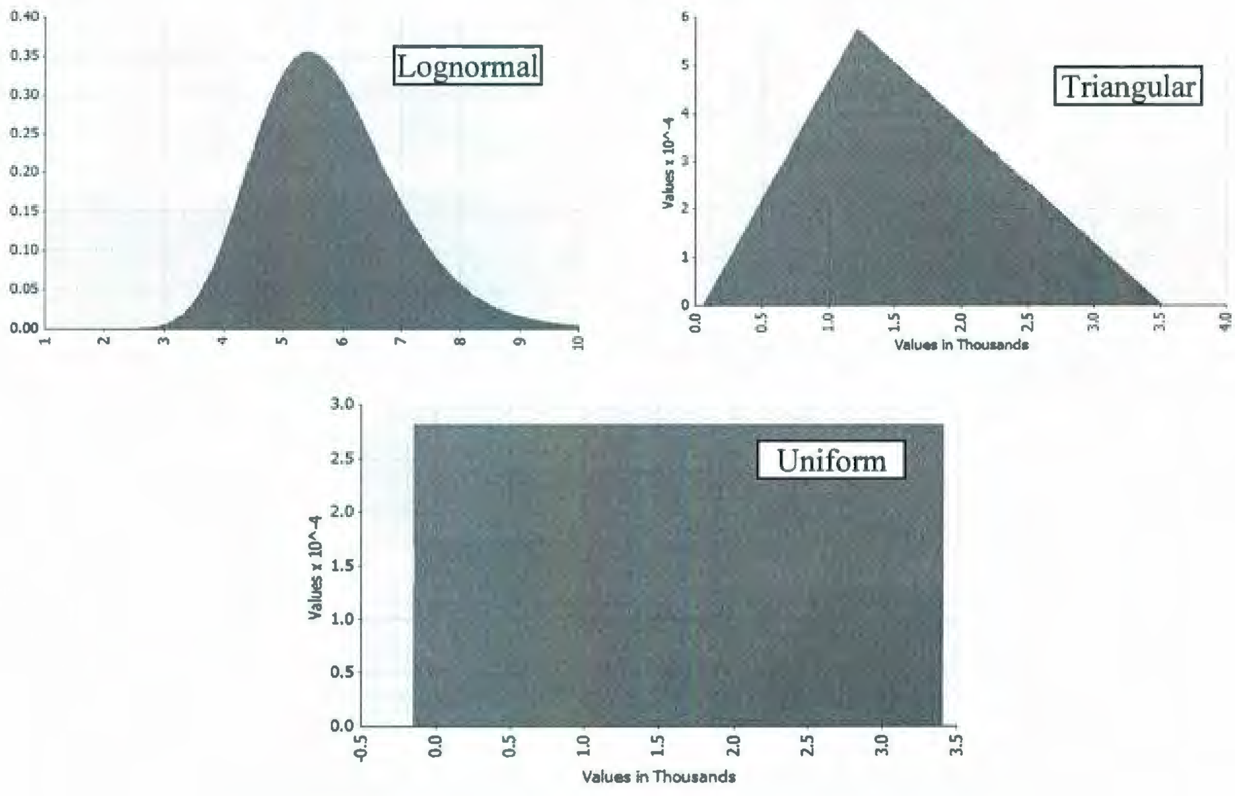

Figure 4.4 PAH Concentration Distributions for Naphthalene

The concentrations of pollutants at the discharge point, C_o in μg/l were taken from Table 2.3. To capture the uncertainty in the data, three different types of distributions were considered in the study: lognormal, triangular and uniform. The concentrations of the PAH chemicals under these three different scenarios are shown in Table 4.4. The distributions' data were extracted from the literatures discussed in Chapter 2.

Table 4.5 shows the parameters used in this study. The details references of these parameters were discussed in Chapter 3 and will be discussed in this chapter.

Table 4.5 Input Parameters and their Characterization for the Model

Model Parameter	Characterization
Effluent discharge rate (m^3/s)	0.212
u (ambient current velocity, m/s)	LN (-3.29, 0.96)
v (Horizontal diffusion velocity, m/s)	0.013
K_z (Vertical diffusion coefficient, m^2/s)	0.012
x (Horizontal length of consideration, m)	100
BCF (Whole fish bioconcentration factor, L/kg)	LN (16.145, 72.682)
F_{epr} (edible part of fish %)	LN (4.36, 0.036)
F_L (Fraction lipid content of fish)	LN (1.139, 1.032)
FIR (Fish ingestion rate, g/d)	LN (0.45657, 4.1748)
BW (Body weight, kg)	LN (0.7321,4.9466)
AT (Averaging time, days)	70×365
F_r (Fraction of contaminated fish ingested, %)	50
EF (Exposure frequency, days/yr)	350
ED (Exposure duration, yr)	30

Figure 4.4 shows the distributions for Naphthalene and their Alkylated homologues. The nature of distributions for these PAH concentrations are not well defined in the literature. In order to eliminate the distribution uncertainties three types of distributions were considered. Lognormal distributions have a central role in human and ecological risk assessment as many physical, chemical, biological and toxicological processes tend to create random variables that follow lognormal distributions (Hattis and Burmaster, 1994). On the other hand the triangular distribution is suitable for a rough approximation to a random variable with an unknown distribution. The uniform distribution does not occur commonly in nature, but as the random number generators in simulation software often built on this, the study also considers this.

The dilution model in equation 3.13 was used for the study. The variables for the dilution are the horizontal diffusion velocity *(v)*, the effluent discharge rate *(Q)*, the horizontal length of consideration *(x)*, and the ambient current velocity *(u)*. The variations of the contaminant concentrations with ambient sea water velocity and discharged velocity are shown in Figures 4.5 and 4.6 respectively. Both these figures show that the dilution ratio is highly variable in the ambient sea water and with respect to the discharge water speed. The uncertainty of the ambient sea water was incorporated by using a lognormal flow velocity in m/s of (-3.29, 0.96). Due to the limited data on the offshore produced water platforms, for conservative analysis the effluent discharge rate of 0.212 m^3/s was considered for the risk analysis.

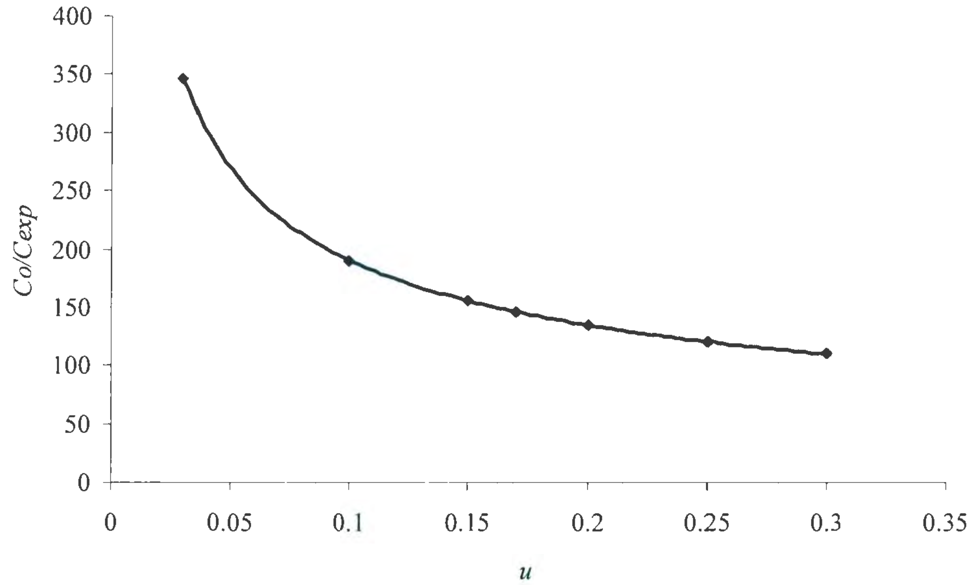

Figure 4.5 Variations of the Concentration Ratio with Ambient Flow

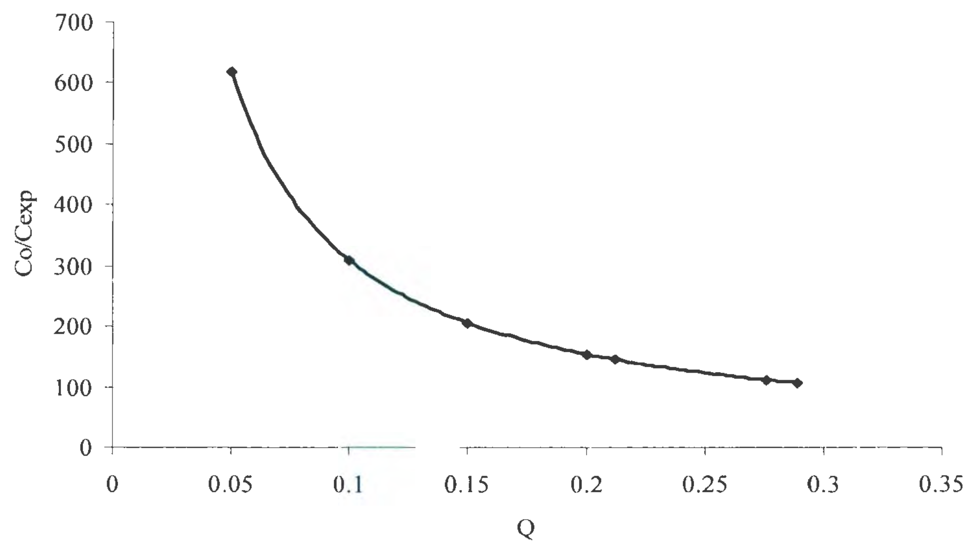

Figure 4.6 Variations of Concentration Ratios with Produced Water Flow

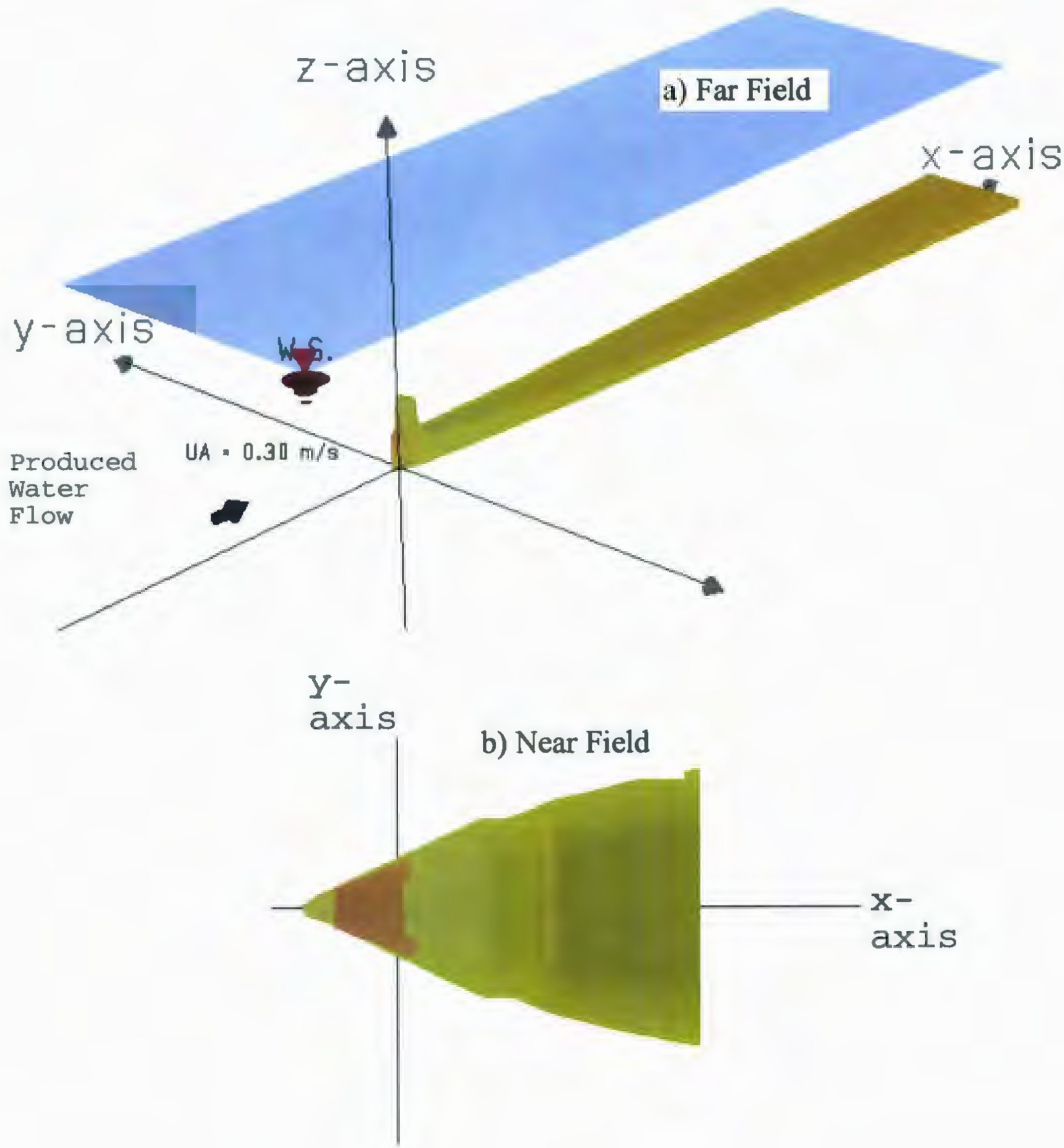

Figure 4.7 Dilution of Naphthalene by using the Cornell Mixing Zone Expert System

Figure 4.7 shows a typical dilution profile for the study for Naphthalene. It can be observed from Figure 4.7 (b) that the near field dilution is predominant for the PAHs discharge.

From equation 3.14 the total amount of PAH contaminants were calculated. The bioavailable factors (*BAF*) for PAHs were considered as 1 (100% bioavailable). For contaminants like metals in produced water these *BAF* need to be adjusted as they are not 100% bioavailable. The bioconcentration factors (*BCF*) also will be different for different contaminants. Depending on the availability of the data they can be used as either deterministic or probabilistic inputs.

Equation 3.15 determines the total amount of PAHs accumulated in a marine fish. The PAH contaminants will accumulate mainly on the edible portions of the fish. From statistical analysis the fraction lipid concentration (F_L) was used as a lognormal distribution of (1.139, 1.032) as shown in Figure 4.8. The edible part of the fish excludes the bones, gills and the external skin of the fish.

The ratio between the weight of the edible part to the weight of whole fish (F_{epr}) in equation 3.16 was also considered a lognormal distribution of (4.36, 0.063).

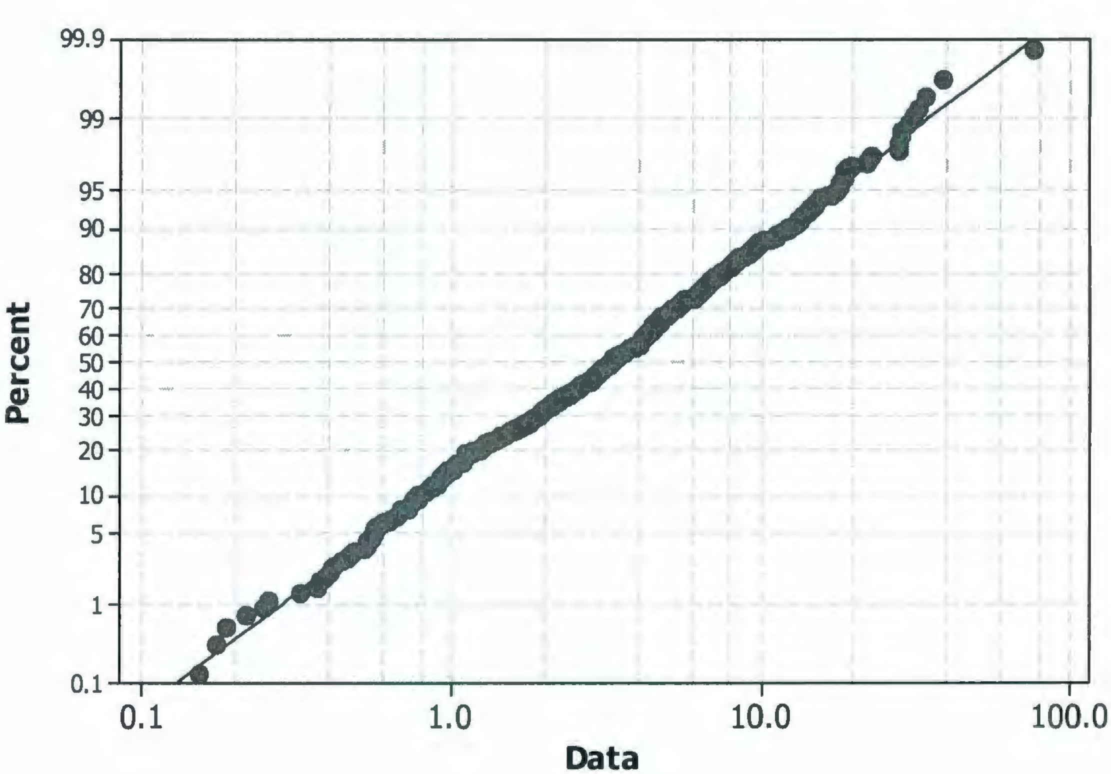

Figure 4.8 Lognormal Probability of Lipid Percent in Fish

The chronic daily ingestion of PAHs to human health was estimated by using equation 3.18. For the daily ingestion calculation from other produced water contaminants gastrointestinal (*GI*) absorption factors may be considered. Especially for heavy metals the GI factors are important as they may be absorbed through gastrointestinal tracts. For PAHs the *GI* factors were not considered as the cancer slope factors of PAH compounds are based on the administered dose, not on the absorbed dose. If sufficient data are available, the differences in absorption from the medium of exposure in the PAHs toxicity study from which the cancer slope factor was derived, and absorption from fish can be adjusted.

From the questionnaire survey the lognormal fish ingestion rate (*FIR*) of (0.45657, 4.1748) was estimated which was used for the intake calculation as shown in Figure 4.9. This distribution significantly differs from Meinhold et al. (1996) which is shown in Figure 4.10. Meinhold et al. (1996) estimated the ingestion rate for open bay Louisiana, USA. This indicates the local variability of the fish ingestion and the importance of a local survey to determine the accurate ingestion values.

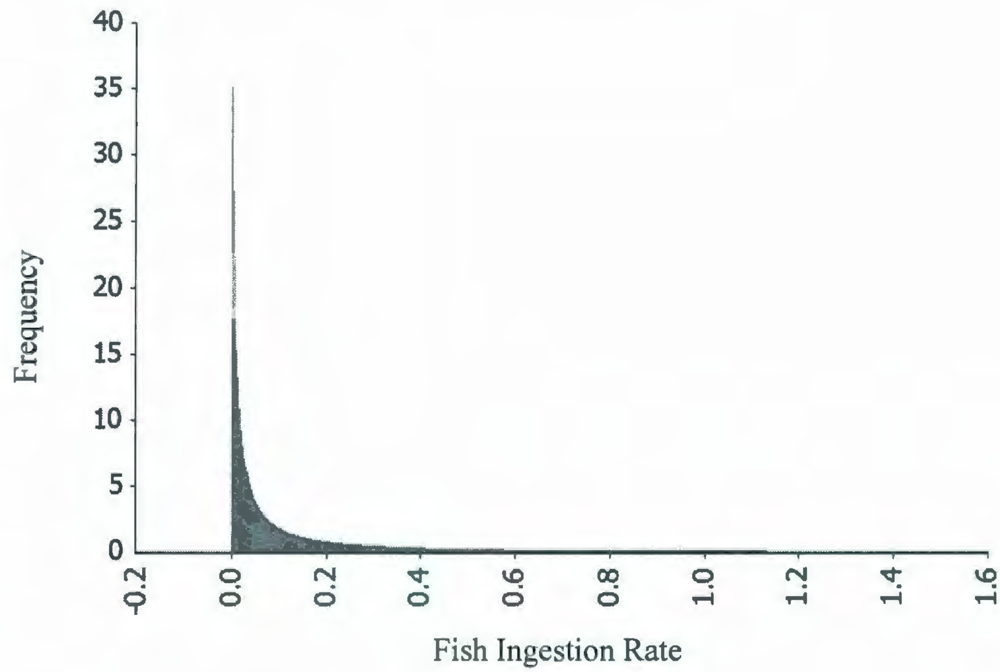

Figure 4.9 Fish Ingestion Rate Estimated from Questionnaire Survey

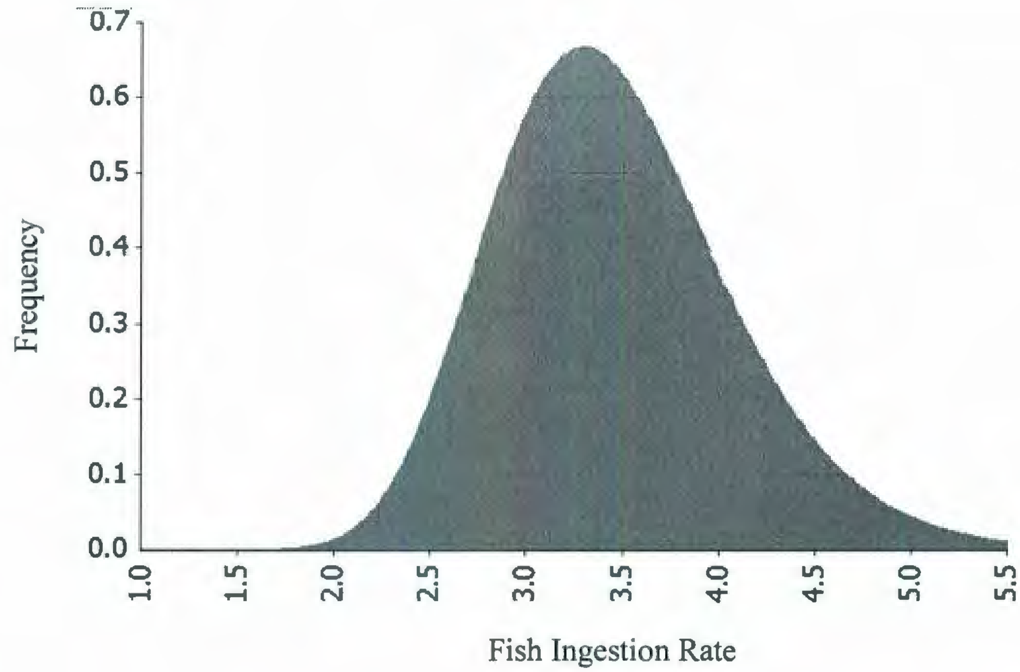

Figure 4.10 Fish Ingestion Rate Estimated by Meinhold et al. (1996)

For the input of human body weight, this study incorporated the uncertainties in the human weight among the different demography by using a lognormal distribution of (0.7321, 4.9466) from the survey. To the best knowledge of the author, for human health risk, estimation the body weight is never considered a variable factor. For risk calculation in different age groups, the survey can be expanded to get more accurate estimation.

The human health hazard quotients (HQ) for each of the chemicals were calculated by using a probabilistic approach with the help of Palisade @Risk software. The individual HQ values for each case and hazard index (HI) values, which were calculated by te probabilistic summation approach, are shown in Table 4.6.

The following assumptions were made for the risk analysis:

- Population demography considered consisted of adults only
- Distribution of contaminants in the dilution zone is steady and homogeneous
- The fishes stay and grow within the dilution zone during the simulation period
- During cooking of fish or fish products, no loss of contaminants occurred
- The growth of fishes and dilution of contaminants remained the same all the year
- Toxicity equivalency factors and reference dose were assumed based on the chemical structure of similar contaminants, if no data were available
- Acceptable risk was estimated as one in a million according to the US EPA

Table 4.6 Hazard Quotients and Hazard Index under Different Scenarios

PAHs Compounds	Case-I: Lognormal	Case-II: Triangular	Case-III: Uniform
Naphthalene & Alkylated Naphthalene	1.88E-05	5.21 E-02	5.33E-02
Phenanthrene & Alkylated Phenanthrene	1.07E-02	5.93E-03	6.07E-03
Benz(a)anthracene	1.70E-03	1.23E-02	4.74E-03
Chrysene	1.18E-03	5.54E-03	2.56E-02
Benzo(b)fluoranthene	2.45E-03	2.53E-03	2.80E-03
Benzo(k)fluoranthene	4.90E-04	6.86E-04	5.72E-04
Benzo(a)pyrene	1.44E-03	1.41E-03	1.42E-03
Indeno(1,2,3-c,d)pyrene	6.73E-03	4.43E-04	4.47E-04
Dibenz(a,h)anthracene	2.83E-03	6.53E-04	6.59E-04
Hazard Index, *HI*=	2.74E-02	8.16E-02	9.55E-02

Figure 4.11 shows the graphical comparison of the estimated hazard values. It shows that Naphthalene and its Alkylated compounds and Chrysene contributed more in Case-II and III scenarios. For example, the lognormal distributions of Naphthalene and Alkylated Naphthalene and Benzo(a)anthracene show higher hazard values. The total HI is higher in Case-III but it is much lower then the maximum accepted value of 1.

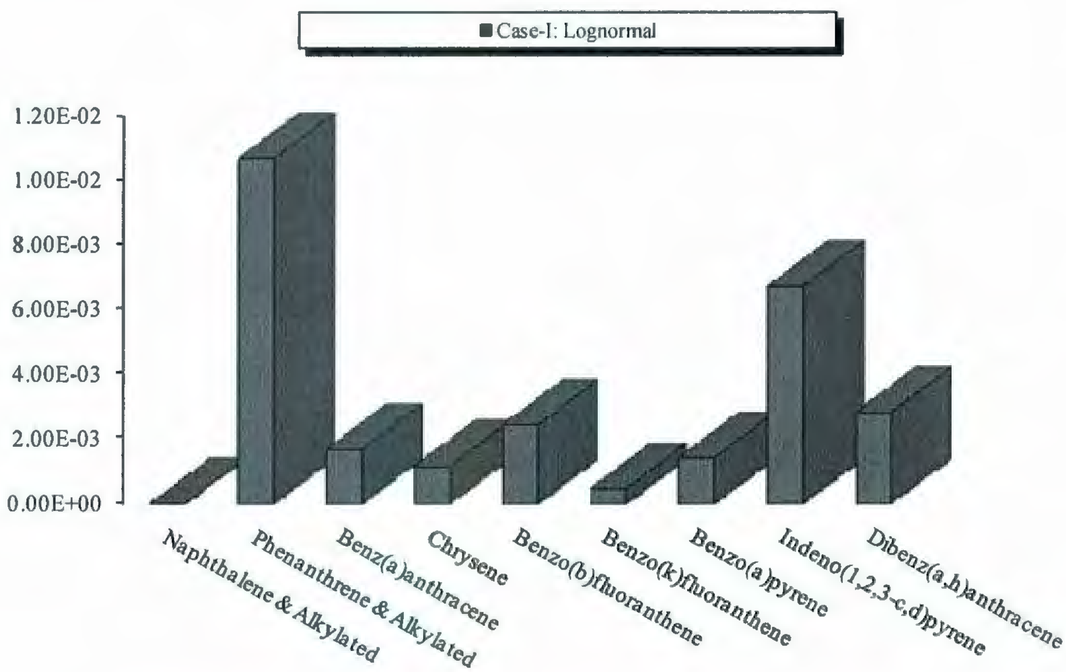

Figure 4.11 Human Health Hazard from PAHs in Case I

The comparison of HI values in the three different case scenarios are shown in Figure 4.12. The figure also confirms the negligible lower hazards of human health from PAHs of produced water. The lognormal concentration considerations show a different hazard pattern than the triangular and uniform case considerations.

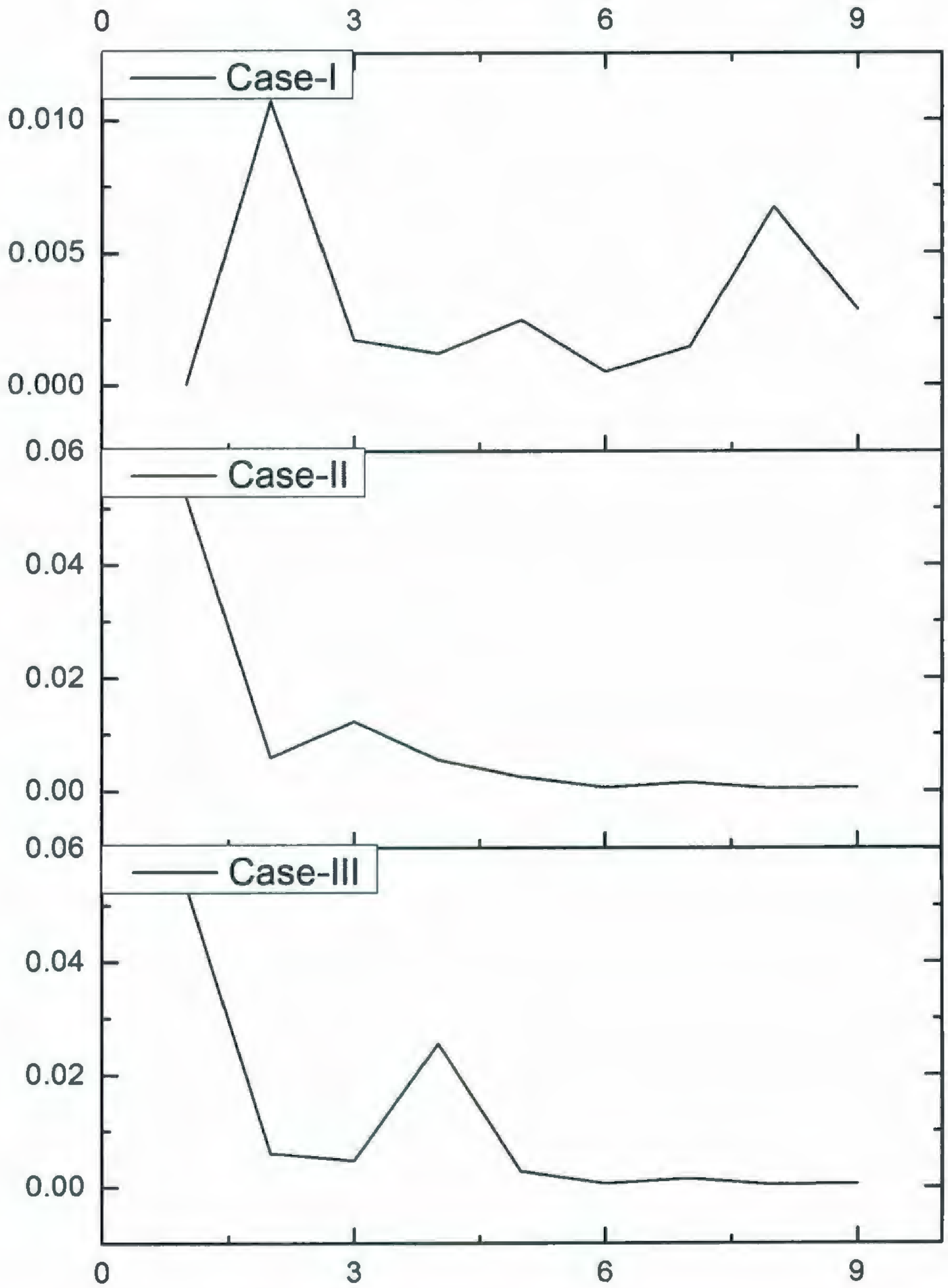

Figure 4.12 Comparison of *HI* under Different Case Scenarios (vertical and horizontal axis denotes frequency/probability of *HI* values and number of data sources respectively)

The cancer risks for individual PAH compounds as well as the total risk for different case scenarios are tabulated in Table 4.7. The risk values in each case are higher than the US EPA acceptable limit 10^{-6}. The risk values in scenarios II and II I were higher than the Case I risks. Naphthalene and Alkylated homologues showed greater risk values then other compounds.

Table 4.7 Cancer Risks under Different Scenarios

PAH Compounds	Case-I: Lognormal	Case-II: Triangular	Case-III: Uniform
Naphthalene & Alkylated Naphthalene	4.52E-09	1.25E-04	1.28E-04
Phenanthrene & Alkylated Phenanthrene	2.54E-06	1.42E-05	1.46E-05
Benz(a)anthracene	2.48E-06	1.80E-05	6.92E-06
Chrysene	2.23E-07	1.05E-06	4.86E-06
Benzo(b)fluoranthene	7.87E-06	8.12E-06	9.00E-06
Benzo(k)fluoranthene	1.00E-06	1.40E-06	1.17E-06
Benzo(a)pyrene	3.15E-05	3.08E-05	3.10E-06
Indeno(1,2,3-c,d)pyrene	3.69E-05	2.42E-06	2.44E-06
Dibenz(a,h)anthracene	1.30E-05	3.01E-05	3.03E-06
Risk value, *R*=	9.55E-05	2.31E-04	1.73E-04
95% percentile Risk=	8.81E-05	8.19E-05	7.63E-05
Mean Risk=	4.18E-05	5.90E-05	6.43E-05

The *95*-th percentile risk values in all cases exceeded the acceptable limit. So the conservative approach under the model assumptions shows risk of human health from PAHs intake through fish ingestion.

Figure 4.13 shows that the cancer risk is higher in scenario II and III for Naphthalene, Phenanthrene and their Alkylated homologues.

The risk values compared to other human health risk assessments from produced water (Chowdhury et al., 2004) show PAH compounds contributes greater amount of risks then Cadmium, Zinc, Benzene, Toluene and Phenol.

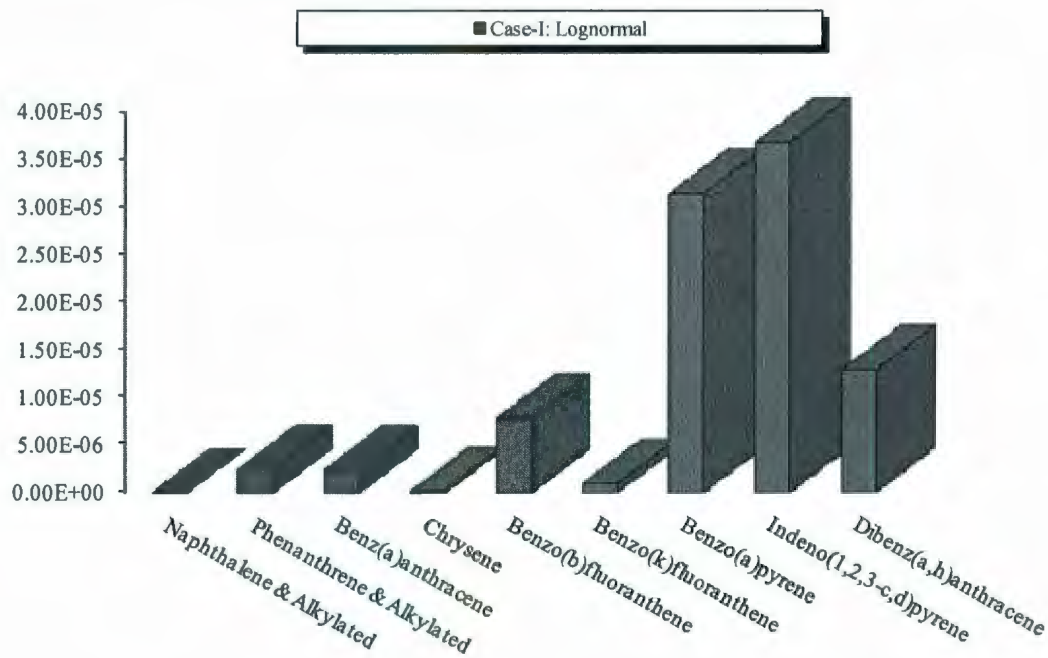

Figure 4.13 Human Health Risk from PAHs in Case I

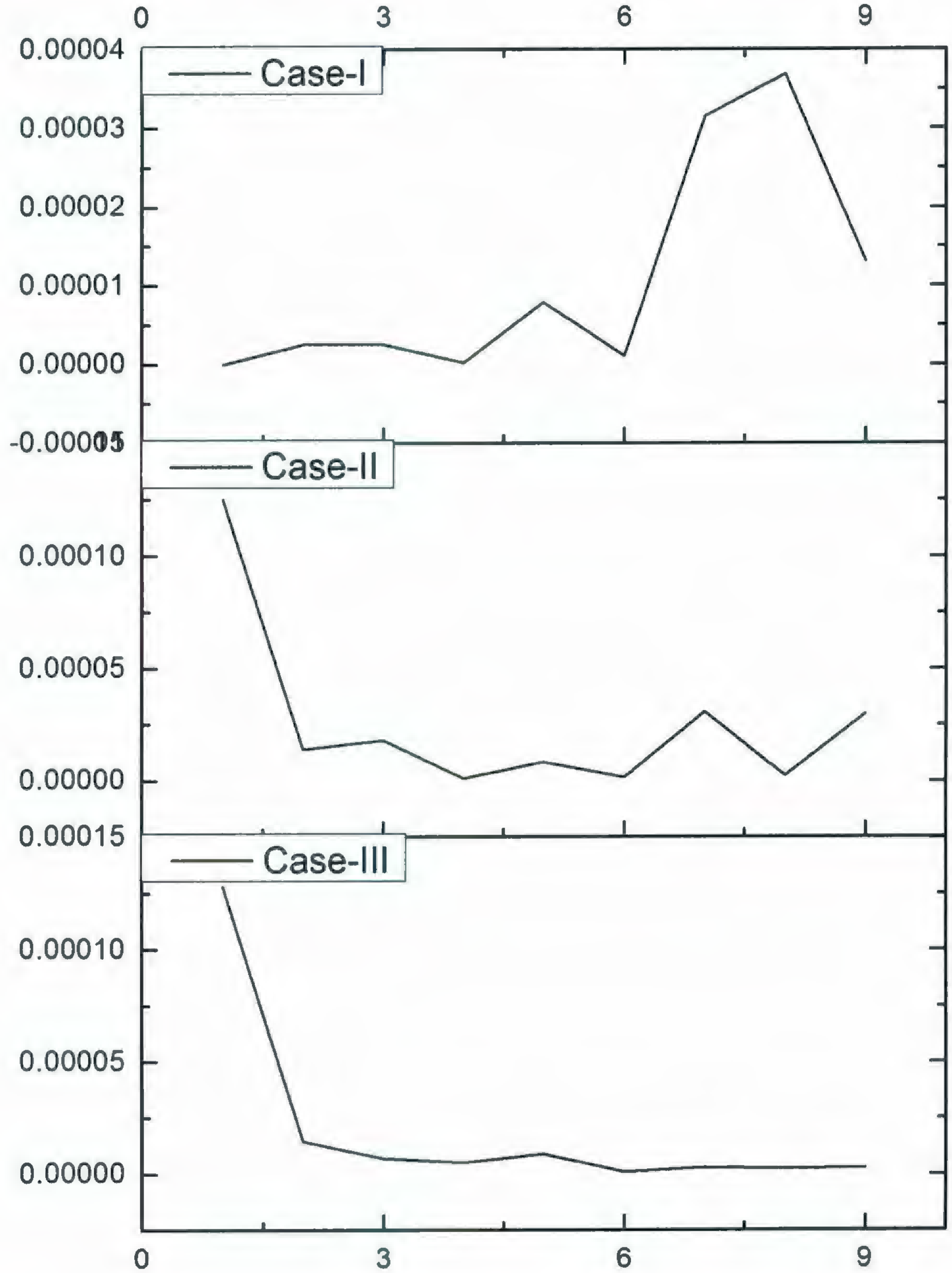

Figure 4.14 Comparison of Risks under Different Case Scenarios (vertical and horizontal axis denotes frequency/probability of *risk* values and number of data sources respectively)

The individual risk values of different PAHs compounds under different case scenarios are shown in Figure 4.14. The lognormal PAHs concentrations showed significant dissimilarities than the other two case scenarios as like the hazard estimations. The exceedence of risks values from the US EPA acceptable limits for different cases are shown in Figure 4.15 (a, b and c for lognormal, triangular and uniform respectively).

Figure 4.15(a) shows that only two PAH compounds exceed the acceptable limit. In case II three PAH compounds and in case III one PAH compound exceeds the limit. These indicated that generally the risks values were within the US EPA limit.

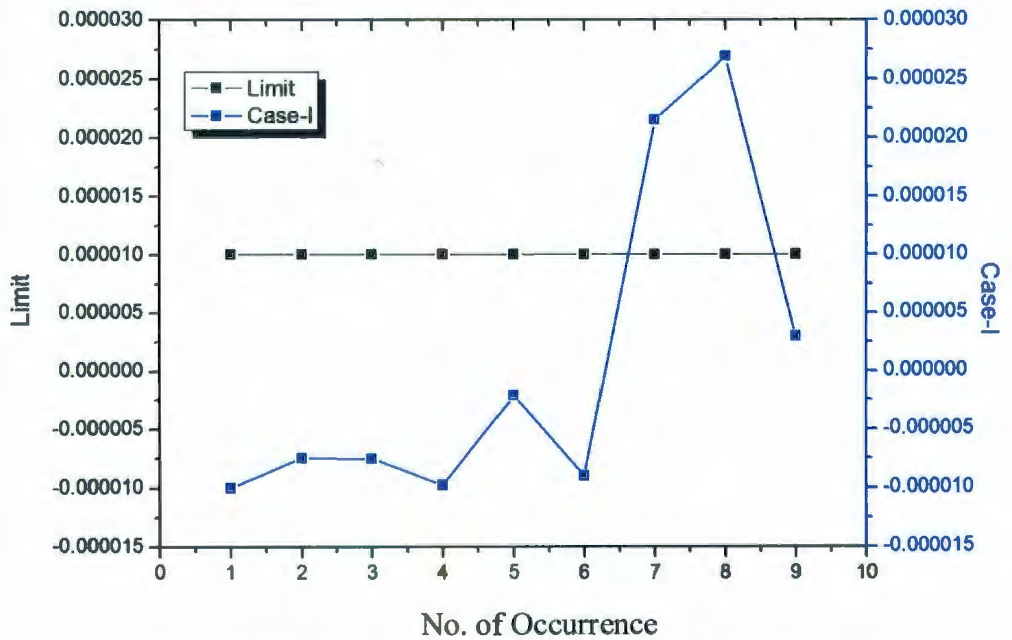

Figure 4.15 (a) Exceedence of Risk in Lognormal Distribution (Case-I)

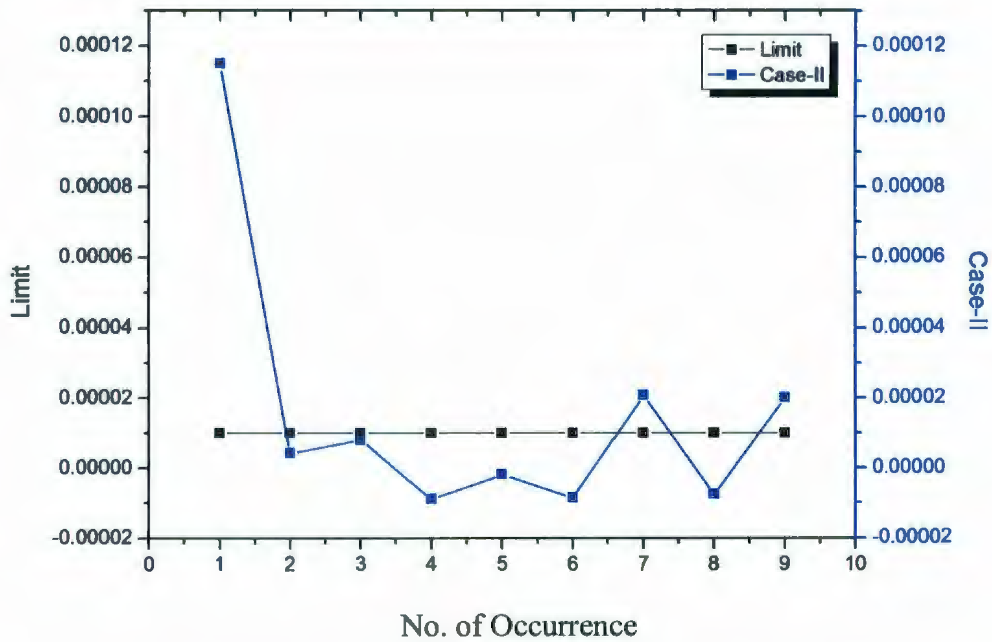

Figure 4.15(b) Exceedence of Risk in Triangular Case (Case-II)

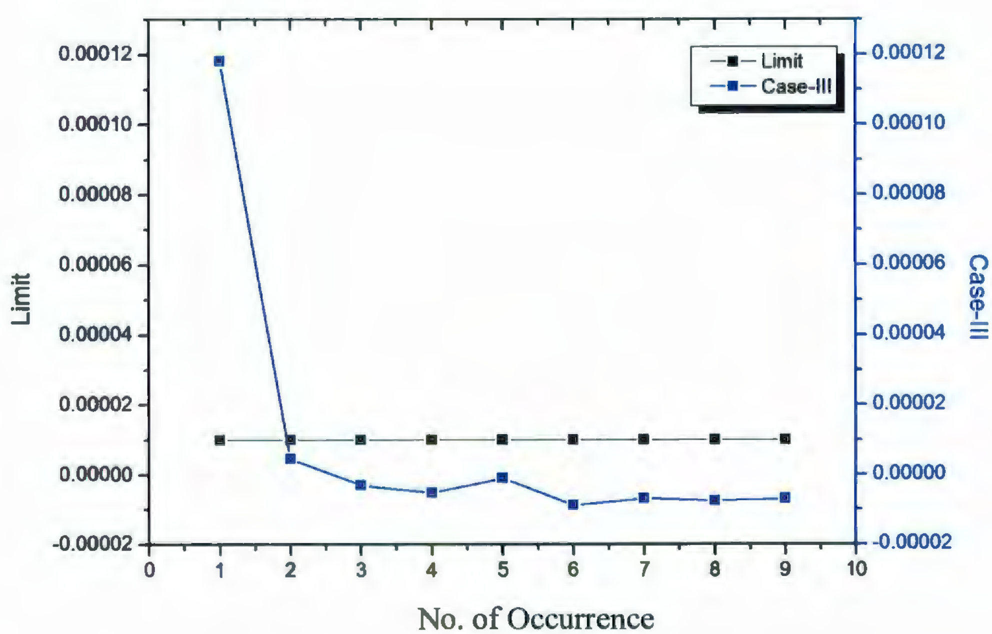

Figure 4.15 (c) Exceendence of Risk in Uniform Case (Case-III)

4.4 Sensitivity Analysis of Deterministic Parameters

In Table 4.5 on Page 89 some model parameters were considered as deterministic values as enough data were not available to establish a distribution pattern. In the absence of detailed information their uncertainties cannot be associated in the model by using the probability distributions. In order to understand their uncertain nature, sensitivity analysis were performed.

Sensitivity analysis is used to determine how 'sensitive' a model is to changes in the value of the model parameters (Breierova and Choudhari, 2001). It is usually performed changing the parameters to see how the model behaviour responds to changes in the parameter values. It is a useful tool for model evaluation and helps to build confidence in the model by studying the parameter uncertainties. Sensitivity analysis tries to indentify what source of uncertainty weights more. The US EPA prescribes sensitivity analysis as a tool to ensure the model quality (US EPA, 2003).

Sensitivity analysis can be performed in different ways: local methods, sampling techniques, a method based on emulators, a screening method, variance methods, high dimensional model representations etc. Details of these methods can be found elsewhere (Grievank, 2000; Oakley and O'Hagan, 2004; Cacuci et al., 2005). Within the scope of the study the sampling based sensitivity analysis were performed in order to assess the data uncertainty of the deterministic model parameters. In the sampling based sensitivity analysis, the model was executed repeatedly for combinations of values, samples from the known values of the input factors (Helton et al., 2006). For simplification, the screening method, which is a special type of sampling technique, was used for this study.

In this study seven deterministic values were used, as shown in Table 4.8. Among these parameters, v, K_z, and ED values are constant in nature. So their ranks in the sensitivity analysis were considered zero and they were excluded from the analysis.

In order to perform the sensitivity analysis, the other parameter deterministic values were varied in two different values: high and low. The risk analysis was then performed by using the high and low variations.

Table 4.8 Parameter Estimation for Sensitivity Analysis

Model Parameters	Rank	Model Value	High Estimation	Low Estimation
Effluent discharge rate (m^3/s)	1	0.212	0.289	0.185
x (Horizontal length of consideration, m)	2	100	500	60
F_r (Fraction of contaminated fish ingested)	4	50%	65%	30%
EF (Exposure frequency, days/yr)	3	350	350	250

Among the other parameters, the effluent discharge was considered the most important, as the pollutant concentration and dilution depend on it. So it was ranked as 1 and the high and low estimation of discharge were considered from literature review as, 0.289 and 0.185 (from the ranges, as discussed in Section 3.5) respectively.

The horizontal length considered is an important factor for dilution of the pollutants. It can be varied up to 1000 m. For the Grand Banks region, the ambient current is high and weather is windy. So a high and low estimation was considered as 500 and 60 m (from the ranges, as discussed in Section 3.5) respectively. This parameter was ranked as 2.

The fraction of ingested fish, (F_r) was considered as 50% in this study. To assess the sensitivity of this data, analysis was done by using two different scenarios: high (F_r value: 65%) and low (F_r value: 30%). It was ranked 4 according to the importance.

Exposure frequency is another important parameter which directly correlates with health risk. In this study the conservative high estimation of 350 days was considered. So the sensitivity was checked only for low estimation of 250 days and it was ranked as 3.

Risk analysis was then performed for the combinations of high and low estimations. The combinations of runs were done according to Table 4.9. These combinations would produce $4^2=16$ runs. By applying the screening method, the combinations of high values of each parameter and low values for others were considered, which produced 4 runs as shown in the Table 4.9.

Table 4.9 Parameter Combinations for Risk Analysis

Rank→	1	2	3	4
Run-1	High	Low	Low	Low
Run-2	Low	High	Low	Low
Run-3	Low	Low	High	Low
Run-4	Low	Low	Low	High

With these four combinations risk analysis were done and the results of estimated risks are shown in Table 4.10.

Table 4.10 Risk Estimation with High and Low Values

Run	Case-I	Case-II	Case-III
Run-1	4.01E-06	2.80E-05	2.85E-05
Run-2	5.22E-05	3.65E-04	3.71E-04
Run-3	8.77E-06	6.13E-05	6.23E-05
Run-4	1.35E-05	9.48E-05	9.64E-05

From the Table 4.10 it can be observed that in all runs, Case-I produced lower risks than Case-II and III. Except the Run-1 and Run-3 for Case-I, all other estimations exceeded the US EPA acceptable limits. The graphical comparison for the estimation is shown in Figure 4.16. The figure revealed that, for Run 1, 3 and 4, the risk estimation followed the similar patterns. Run 2 (variations of horizontal dilution length) affected significantly the risk values. A high fraction of ingested fish produced the next highest risk estimation in Run 4. In Run 1, the higher effluent discharge rate had a minimal affects on risk estimation.

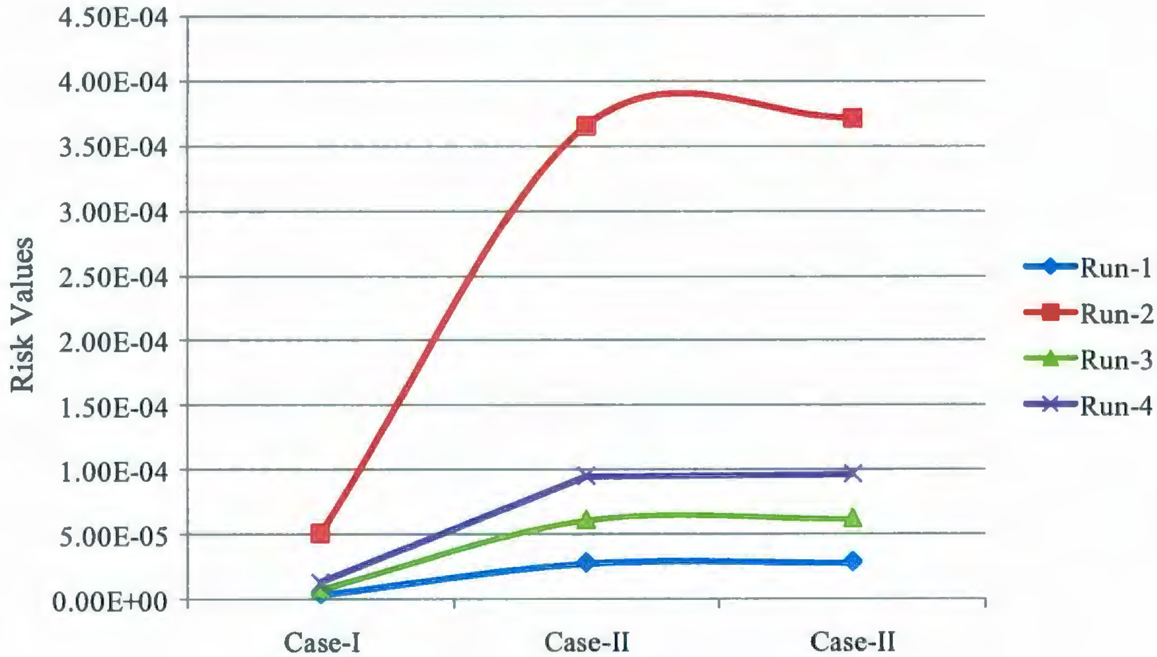

Figure 4.16 Sensitivity Analyses of Parameters

From the sensitivity analysis it can be concluded that, dilution has a greater impact on risk estimation. The fraction of contaminated fish and exposure frequency to contaminated fish are also important. Further investigations can be done on these parameters in order to establish their distribution from data collection and/or survey.

4.5 Comparison of Results with the DISSPROWM

The risk assessment values were compared by using the DISSPROWM tools. The default values of the tools were modified as necessary. The DISSPROWM tools only accept deterministic values and provide output as the same. For PAH compound concentrations, mean values were considered for the DISSPROWM input concentrations. The results showed the non-carcinogenic risk was insignificant (negligible risk) however for carcinogenic risk the total risk value was 3.07E-03 which is much higher than the three case scenarios. The comparison was made with one case, study case-II for conservative assessment. Table 4.11 summarize the individual risk estimation values.

Table 4.11 Cancer Risk Assessment by using the DISSPROWM

PAHs Compounds	Risk	Study Case-II
Naphthalene & Alkylated Naphthalene	2.73E-04	1.25E-04
Phenanthrene & Alkylated Phenanthrene	4.64E-05	1.42E-05
Benz(a)anthracene	1.10E-04	1.80E-05
Chrysene	1.39E-05	1.05E-06
Benzo(b)fluoranthene	1.18E-04	8.12E-06
Benzo(k)fluoranthene	7.41E-05	1.40E-06
Benzo(a)pyrene	1.10E-03	3.08E-05
Indeno(1,2,3-c,d)pyrene	6.73E-03	2.42E-06
Dibenz(a,h)anthracene	2.64E-04	3.01E-05

The comparison of the Case-II (triangular distribution) with the DISSPROWM shows that, the deterministic values of risks are greater than the probabilistic analysis. Figure 4.17 shows the comparison in the same vertical scale.

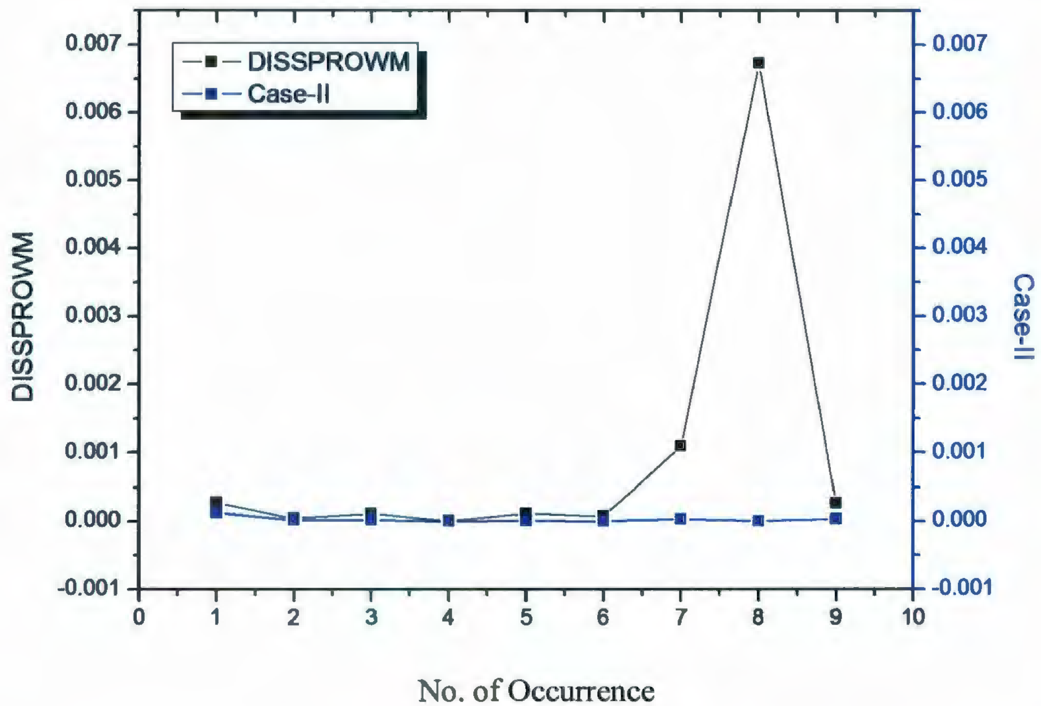

Figure 4.17 Comparisons of Study Results with the DISSPROWM

The difference in the risk estimation may be caused due to the following reasons:

- The DISSPROWM model incorporates deterministic input values for different parameters
- The dilution model adopted in the DISSPROWM is different than the one adopted in this study

- In this study several new methodology adopted for parameter estimation and the analysis was done by probabilistic approach

4.5 Summary

In this chapter the proposed methodology was applied in a hypothetical case for an offshore oil field in Atlantic Canada. The Hibernia oil field has become an important economical factor for the region. The diversity of the marine species and birds also extends the ecological importance of the field location. Three PAH compound distribution scenarios were considered to assess the human health hazard and cancer risks by using a probabilistic approach. The hazard values were found to be significantly lower than the acceptable limit. The total cancer risk under each scenario was found to be higher than the acceptable limit. The results showed that, though the non-carcinogenic risk is negligible, for the long term carcinogenic risks, it may poses health risks. The sensitivity analysis was done to assess the data sensitivity of the deterministic model parameters. The analysed results were compared by using the DISSPROWM tools which provided the deterministic values. The deterministic analyses showed greater risks than the probabilistic analyses. Discussions on results are provided in the following chapter.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The conclusions of the proposed methodology for human health risks from offshore produced water, and discussions on questionnaires of the survey on fish consumptions have been presented in this concluding chapter. The research was carried out to assess the human health risk from the produced water and composed of the following components: i) development of a fish growth model by using a method suitable for the produced water exposed area, ii) development of a human health risk assessment model for PAHs using probabilistic approaches, iii) conducting a questionnaire survey in the local communities to estimate the fish intake trends, iv) applying the methodologies by using data from the literature and information from the questionnaire survey; and v) comparing the results with the that of Decision Support System of Produced Water Management (DISSPROWM) tool.

In the focus of the above objectives, the following are the conclusions of this study:

1. Produced water contaminants fall under three major categories: metals, aromatics and radioactive materials. Among the aromatic compounds PAHs are considered most toxic and they are persistent in nature. So far to the best knowledge of the author, no study done before to assess the risk from PAHs for human health originated from offshore produced water. Data regarding the offshore platform are inadequate which increases the uncertainties for risk estimation.
2. The most popular risk assessment methodologies were proposed by the US EPA which considers the pollutant concentrations of fish tissue for oral ingestion. The fish ingestion rate (FIR), exposure duration(ED), exposure frequency (EF), fraction of contaminated fish (F_r), body weight (BW), averaging time (AT) and other related parameters were incorporated with the proposed risk assessment methodology. From the conservative point of view, ingestion of 50% contaminated fish from marine sources were considered as, i) all the ingested fish may not came from the same source, ii) all the marine fish may not grow in the same contaminated sources, and iii) people may not always be exposed to contaminated fish.
3. For Atlantic Canadian region no data is available for sea fish ingestion. A questionnaire survey was prepared and the survey was conducted by using a popular online survey site Zoomerang.com, which allows users to create and send surveys and analyze results on-demand. The survey link was circulated among the graduate students, engineering students, and local communities by using Facebook and e-mail. Appendix-A shows the questions for the survey.

4. In total 62 respondents completed the survey reporting over 215 people in different households and family sizes. The fish ingestion rate was determined from the survey as a lognormal distribution of (0.45657, 4.1748). 95% of the people bought fish from supermarket, 35% also bought fish from the local market or ate fish in restaurants. 49% of people considered the source of the fish before they buy it. 81% of the respondents thought that fishes they ate were very safe (39%) to somewhat safe (42%). 50% of the respondents heard at least once that fishes available in Canada were not safe. These and some general comments from the respondents indicated that there was concern among the people regarding the fish safety. The survey also showed that people think pregnant women and children under five years of age are more vulnerable to fish contamination. 18% only thought it might affect to adult people as well. These indicate there is a possible need for more education regarding risk exposure.
5. The two types of popular fish growth models; the VBGM and the Gompertz model were considered in this study. The growth parameters were estimated for the common marine fishes grown in Atlantic Canada. The length at age and weight at age model were developed by using statistical analysis. The models were fitted against published data and result showed the VBGM provided more reliable output for fish growth models for the selected species.
6. The proposed model was applied in a hypothetical case study area for an offshore oil platform of Hibernia, Grand Banks, Canada. Three scenarios were considered for different PAHs compounds concentrations which incorporated the data

uncertainties. Probabilistic inputs were used for PAH concentrations, bio-concentration factors (*BCF*), current speed, fraction of lipid concentrations in fish (F_L), ratio between edible and non-edible parts of fish (F_{epr}), Fish ingestion rate (*FIR*), and Body weight (*BW*). The predicted human health cancer risk was found to be above the US EPA acceptable limit. The study output was compared by using the decision tool DISSPROWM which provided the deterministic outputs. The deterministic values were found to be more than the probabilistic values. The results were compiled in Chapter 4.

7. The calculated risk values may have been higher due to the i) lack of PAH concentrations data, ii) lack of data regarding the metabolism of PAHs to fish tissue and subsequent absorption by the human body, iii) uncertainties associated with the dilution model, iv) uncertainties associated in the fraction of contaminated ingested fish and v) lack of information about slope factors of PAH compounds.

5.2 Recommendations

For the future research on this study direction, the following recommendations are made:

1. The produced water concentrations for PAHs were collected from different literatures. Laboratory analysis of produced water can provide more realistic and better estimation for the concentrations. It can also help to understand the

accumulation of contaminants in fish tissue, fate and dilution of the produced water.

2. The model can be applied for all the contaminants of produced water. This will provide deep understanding about the total risks from produced water: both for the environment and human health. The data uncertainty can be handled by using a probabilistic approach or fuzzy based approach. Fuzzy based risk analyses are gaining popularity in industrial as well as in human risk analysis.
3. The sensitivity analysis revealed that the dilution of the produced water had a greater impact on the risk estimation. The fraction of contaminated fish and exposure frequency were the next two important deterministic factors. A further study could be carried out to establish their distributions.
4. The questionnaire survey could be expanded to more people, which would provide more realistic data for the fish ingestions as well as other model parameters such as body weight, demographic groups at risk etc.
5. The simple dilution model used in this study can be replaced by the CORMIX or DREAM which can estimate more realistic real field dilution and dispersion. The dilution parameters can be tested by using the Autonomous Underwater Vehicle (AUV) available at MUN.
6. The student version of @Risk software was used for risk analysis, which has some limitations, such as limited numbers of simulation run, customization of output etc. The use of the industrial version of @Risk would provide more flexibility for risk analysis.

5.3 Thesis Contributions

Followings are the summary of outcomes in this research.

1. Human health risk assessment of PAH originated from offshore produced water by using probabilistic and deterministic approach.
2. Compared two different fish growth models: von Bertalanffy growth model and Gompertz growth model for the fish length-weight estimation exposed to offshore produced water.
3. Conducted questionnaires surveys to assess the marine fish consumptions in the local regions. Probabilistic distributions of fish ingestion rate and body weight were established from the survey. The survey also provided important information regarding the fish availability, risk education and other related information.
4. A framework of human health risk assessment was developed and applied on a hypothetical case study. The model parameters were estimated to be represented by a probabilistic distribution to incorporate the uncertainties.

Publication Lists

The following publications and presentation were published/presented during the course of the Master of Engineering Program related to this research.

Journal Paper

- Chowdhury, K., Husain, T., Veitch, B., and Hawboldt, K, 2009, Probabilistic Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Produced Water, Journal of Human & Ecological Risk Assessment, Taylor & Francis, 15(5):1049-1063

Conference Papers

- Chowdhury, K. and Husain, T., 2009, Application of Decision Support System for Produced Water Management (DISSPROWM) for Human Health Risk Assessment, CSCE 2009 Annual General Conference, St. John's, Newfoundland and Labrador, May 27-30
- Chowdhury, K., Husain, T., Veitch, B., and Hawboldt, K, 2007, Probabilistic Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Produced Water, International Produced Water Conference: Environmental Risks and Advances in Mitigation Technologies, St. John's Newfoundland, October 17-18

Posters

- Mahmoud, N., Chowdhury, K, Husain, T., and Hawboldt, K., 2007, Partitioning of Aromatics in Water, International Produced Water Conference: Environmental Risks and Advances in Mitigation Technologies, St. John's Newfoundland, October 17-18

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Appendix: Questionnaire Survey

Fish Consumption Survey
Faculty of Engineering & Applied Science
Memorial University of Newfoundland

Interviewer's Name: Age: Sex: M/F
Date:
Time:
Location:

Thank you for taking the time to answer these questions about the information regarding fish consumption. The survey should take about 12 minutes. No name or address will be used in any where except for record keeping purpose. If you have any concern about privacy issue or need any clarification/information please mail to: email-id(at)mun.ca.

(INSTRUCTIONS TO INTERVIEWER IN PARENTHESIS/CAPS)
1.) Do you and your family eat fish? By 'fish' we mean any type of sea foods.
- ☐ Yes
- ☐ No

(IF NO THANK AND CONCLUDE INTERVIEW)

(If YES)
1a. What part of the fish do you eat/use? (READ AND CHECK ALL THAT APPLY)
- ☐ Whole fish
- ☐ Heads
- ☐ Organs
- ☐ Fillets

1b. How many members in your family?
- ☐ Adult_______________
- ☐ Child (below 6 yrs)______________
- ☐ Child (6-10 yrs)________________

1c. Are you member of any ethnic group or non-Canadians?
- ☐ Yes
- ☐ No
- ☐ Don't want to disclose

1d. How do you cook the fish? (READ AND CHECK ALL THAT APPLY)
- ☐ Broil
- ☐ Bake
- ☐ Fry
- ☐ Stew
- ☐ Make fish soup
- ☐ Raw
- ☐ Dried

2.) How often do you/your immediate family eat fish each week? (CHECK ONLY ONE)

- ☐ Less than once/wk
- ☐ 1-2 times/ wk
- ☐ 3-4 times/wk
- ☐ 4-5 times/wk
- ☐ 5-6 times/ wk
- ☐ every day

3.) How much fish you usually buy? (CHECK ONLY ONE)

- ☐ Less 300 gm/wk
- ☐ 300-600 gm/wk
- ☐ 600-1000 gm/wk
- ☐ About 1000 gm/wk
- ☐ More then 1000 gm/wk
- ☐ Other, please mention amount____________________gm/wk

4.) What are the main reasons that you/your immediate family eat fish? (CHECK ALL MENTIONED)

- ☐ It is good for you
- ☐ Tastes good
- ☐ Price is not expensive
- ☐ Heritage/tradition
- ☐ Like to catch and eat
- ☐ Other: ________________________________

5.) Are there any kinds of fish that you /your immediate family do not eat?

- ☐ Yes
- ☐ No

If yes, which ones?

____

Why?

____

6.) Where do you get most of the fish that you and your immediate family eat? (CHECK ORDER MENTIONED)

- ☐ Local fish market
- ☐ Supermarket
- ☐ Restaurant
- ☐ From friend and family who catch fish

Other: ________________________________

7.) How do you decide on which fish to buy?

- ☐ Price
- ☐ Type of fish
- ☐ Where it comes from
- ☐ The kind of store where you buy it
- ☐ You know the owner of the store that sells fish
- ☐ Other: ________________________________

8.) How do you know if a fish that you catch or buy is healthy to eat? (CHECK ALL MENTIONED)

☐ By the color
☐ By the smell
☐ By the fish gills
☐ Where you buy it
☐ Where you fish
Other: ________________________________

9.) In general, how safe do you think the fish in the Canada is? (CHECK ONE)

☐ Very Safe
☐ Somewhat safe
☐ Not safe
☐ Don't think about it

10.) Have you ever heard about some fish in the Canada that is unsafe to eat?

☐ Yes
☐ No
If so can you tell me what you heard?________________________________

11.) Who should be most careful about eating fish that is contaminated? (READ AND CHECK ALL MENTIONED)

☐ Pregnant women
☐ Children less than 5 years old
☐ Teens and children over 5 years old
☐ Men and Women over 18 years old
☐ Older people