DECISION SUPPORT SYSTEM FOR PRODUCED WATER DISCHARGES IN OFFSHORE OPERATIONS

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DECISION SUPPORT SYSTEM FOR PRODUCED WATER DISCHARGES IN OFFSHORE OPERATIONS

by

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Abstract

Offshore Oil and Gas producing platforms discharge produced water into the sea during production operations. This water contains toxic contaminants that are harmful to the marine environment. Produced water is treated before its discharge into the sea to reduce risks to the environment. Despite treatment, produced water contains a certain amount of contaminants that are not feasible to treat before discharge and can cause environmental concern.

The main objective of this study is to develop decision support software with an application to characterize risk of produced water released from offshore platforms during operation. The specific objectives are: (1) development of a database for produced water contaminants; (2) integration of a chemical database with selected initial dilution and subsequent dispersion models; (3) development of a probabilistic fish growth model; (4) development of human health cancer and non-cancer risk assessment methodologies using probabilistic concepts; (5) development of a methodology to estimate the distribution of chemicals in the bones/shell/skeleton and flesh of a fish; and (6) application of the methodologies to a hypothetical case study. A chemical specific approach rather than total toxicity approach was employed to predict exposure concentration. Both deterministic and probabilistic hydrodynamic initial dilution models were used in this research. Monte Carlo simulations were performed in the probabilistic analysis.

The database on chemicals was integrated into the initial dilution and dispersion models for predicting available concentration in the marine environment. This predicted environmental concentration (*PEC*) was converted to exposure concentration (*EC*) by incorporating probability of exposure and bioavailability. The concentration of contaminants in fish tissue was predicted through integrating a fish growth model and is presented in a modular form in the software.

The risk of produced water to human health was based on the methodology of contaminated seafood ingestion. The hazard quotient (*HQ*) for non-carcinogens was predicted through dividing the chronic daily intake (*CDI*) by the reference dose (R_fD). The cancer risk was predicted through multiplying the *CDI* by the slope factor (*SF*). The deterministic and probabilistic analyses for risk assessment were integrated into the software. Risk from radionuclides in produced water was performed in a separate module and integrated with the main database.

This study has introduced a concept of chemical distribution within a fish's body and variability in the lipid contents in the fish. The change in edible parts during the exposure period has been predicted through a probabilistic fish growth model and integrated with the human health risk assessment methodologies.

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a	Fish growth model coefficient
a_1	Coefficient to establish relationship between near field and far field
a_2	Coefficient to establish relationship between near field and far field
$A(p)$	Area under standard Normal Distribution from 0 to p along the abscissa.
b_1, b_2 ,b_3	Huang et al. (1998) initial dilution model coefficients
B	Discharge specific buoyancy flux (m^4/s^3)
c	Fish growth model coefficient
C_0	Concentration of contaminant prior the discharge
C_1	Lee and Cheung (1991) initial dilution model coefficient
C_2	Lee and Cheung (1991) initial dilution model coefficient
C_3, C_4	Horizontal boil location coefficients for near field
C_5	Coefficient to calculate C_4

C_a	Bulk pollutant's concentration at the downstream end of the control volume
$C_{bonerad}$	Radium concentration in bone/shell/exoskeleton (pCi/kg)
C_{D1}, C_{D2}	Constants for calculating distance from boil center to the end of control volume
C_{exp}	Exposure concentration for fish (μg/l)
C_f	Concentration in fish tissue
C_{flrad}	Concentration of radium in fish tissue (pCi/kg)
C_L	Concentration of contaminant in lipid of a fish
C_{rad}	Radium concentration in whole fish (pCi/kg)
C_{s1}	Dilution coefficient for buoyancy dominated near field
C_{s2}	Dilution coefficient for buoyancy dominated far field
C_w	Predicted environmental concentration (PEC).
$C(x,y)$	Predicted environmental concentration (PEC) at point (x,y).
d	Diameter of the exit pipe
d_2	Huang et al. (1998) initial dilution model coefficient
e_1, e_2	Coefficients of curvature parameter (k)
e_3, e_4	Coefficients of Initial Condition parameter (t_o)
$erf(z)$	Error function of z
f_1, f_2	Growth parameters Weight-Length model of a fish
F_o	Jet deterministic Froude Number
F_{epr}	Ratio between the weights of edible parts to the weight of whole fish

F_L	Fraction lipid content in a fish
Fr	Fraction of lipid in fish
g	Acceleration due to gravity (m/s^2)
g_1	Growth rate of fish
h_o	Plume thickness (m) at the end of control volume
$h(x)$	Plume thickness (m) at distance x
H	Depth of the ambient water (m)
I_T	Total radium intake (pCi)
k	Curvature parameter (1/year)
l_b	The buoyancy length scale (m) at which the jet velocity approaches to the ambient velocity
l_m	Length scale (m), a measure for momentum dominated jet with a cross flow
l_M	Measure of the distance where buoyancy becomes more effective than the jet momentum.
l_Q	Measures of direct effect from jet geometry on flow characteristics (m)
L_o	Plume width at downstream end of control volume (m)
L_s	Upstream intrusion length of plume (m)
L_t	Fish length at age t
$L(x)$	Plume width at distance x (m)
L_∞	Asymptotic length at infinitely long period
m	Slope of the fish growth model equation

M	Discharge momentum flux (m^4/s^2)
n	Number of species for which toxicity data for that chemical is available
$N(0,0.12)$	Normally distributed error term with mean 0 and standard deviation 0.12 in the fish growth model
p	Exposure probability
Q	Source volume flux (Discharge rate) [m^3/sec]
S	Dilution
S_{a1}	Bulk dilution at control volume end for BDNF
S_{a2}	Bulk dilution at control volume end for BDFF
S_a	Bulk dilution at control volume end
(SS_{res})	Sum square error
t	Age in year
t_o	Initial Condition parameter
t_1	Initial age of fish when it is exposed to produced water
u	Ambient current velocity (m/s)
u_j	Exit velocity of jet (m/s)
W_O	Initial weight of fish before exposure (g)
W_c	Total accumulated contaminants in a fish (μg)
W_L	Weight of lipid (kg)
W_t	Weight of fish at time t (g)
x	Distance from the end of the control volume along plume centerline
x, y	Edible part and non-edible part of fish

x_b	Horizontal location of boil center from port (m)
x_{b1}	In near field, horizontal location of boil center from port (m)
x_{b2}	In far field, horizontal location of boil center from port (m)
x_{btrans}	Horizontal location of boil center from port (m) for transition regime
x_{D1}	Distance from boil center to the end of control volume (m) for BDNF
x_{D2}	Distance from boil center to the end of control volume (m) for BDFF
x_D	Distance from boil center to the end of control volume (m)
X	Fixed direction in the global coordinate system
y	Distance from the end of the control volume perpendicular to x axis
Y	Direction perpendicular to the X in the same plane for global coordinate system
z	Depth above discharge
α	Entrainment coefficient
β	Model constant for buoyant spreading
$\sigma(x)$	The standard deviation of the concentration distribution across the plume width
θ	Angle between rising jet axis and water surface
φ	Current direction (radian) with respect to the X - Coordinate direction
ρ_a	Ambient water density (kg/m^3)
ρ_e	Effluent density (kg/m^3)
$\Delta\rho_j$	Density gradient between ambient sea water and effluent
ω_{ji}	Regression variable in fish growth model

γ_j	Regression coefficient for iteration in fish growth model
ε_I	Fish growth model error term and
ξ	Proni et al (1994) initial dilution model coefficient for transition regime
η	Proni et al (1994) initial dilution model coefficient for transition regime

List of Abbreviations

ADI	Average Daily Intake
ANWQG	Australian and New Zealand Guideline for Fresh and Marine Water Quality
AT	Averaging time
BAF	Bioavailable fraction
BAT	Best Available Control Technology
BCF	Bioconcentration Factor
BDNF	Buoyancy Dominated Near field
BDFF	Buoyancy Dominated Far field
BPD	Billion barrels per day
BPT	Best practicable Technology
BPY	Billion barrels per year
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
BW	Body weight
CCME	Canadian Council of Ministers of the Environment

CDI	Chronic Daily Intake of non-carcinogen
CDI_C	Chronic daily intake of carcinogen (mg/kg-day)
CF	Conversion factor
CHARM	Chemical Hazard Assessment and Risk Management
C-NOPB	Canada-Newfoundland Offshore Petroleum Board
COD	Chemical Oxygen Demand
CORMIX	Cornell Mixing Zone Expert System
CR_{RAD}	Cancer risk from radionuclides
DFO	Department of Fisheries and Oceans
DO	Dissolved Oxygen
DREAM	Dose Response Effects Assessment Models
EC	Exposure Concentration
EC_{50}	Pollutant's concentration at which 50 % of tested animals is affected
ECOTOX	Eco-toxicology Database
ED	Exposure Duration
EF	Exposure Frequency
ERA	Ecological Risk Assessment
FF	Far field
FPSO	Floating Production Storage and Offloading
FIR	Fish Ingestion Rate (g/day)
FR	Fraction of fish contaminated with produced water

GESAMP	The Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection
GM	Geometric mean
GDP	Gross Domestic Product
GOM	Gulf of Mexico
HCR	High cancer risk
HI	Hazard Index
HLC	Henry's Law Constant
HMSO	Her Majesty's Stationery Office
HQ	Hazard Quotient
IRIS	Integrated Risk Information System
Koc	Sorption Coefficient
K_{ow}	Octanol-Water partition coefficient,
Ksedw	Sediment-Water Partition Coefficient
Kssdw	Suspended Solid-Water Partition Coefficient,
LC_{50}	Pollutant's concentration at which 50 % of tested animals died
LF	Leaching factor
LOAEL	Lowest Observed Adverse Effect Limit
MATC	Maximum Acceptable Tissue Concentration
MC	Monte Carlo
NF	Near Field
NGL	Natural Gas Liquid

NOAEL	No Observed Adverse Effect Limit:
NOEC	No Observed Effect Concentration
NORM	Naturally Occurring Radioactive Materials
NPD	Naphthalene, Phenanthrene and Dibnenzothiophene including their alkyl homologues
NRC	National Research Council
NSCRF	National study of chemical residues in fish
NSPS	New Source Performance Standards
OGP	International Association of Oil & Gas Producers
OOC	Offshore Operators Committee
OSPAR	Oslo and Paris
PAHs	Polycyclic Aromatic Hydrocarbons
PEC	Predicted Environmental Concentration
PNEC	Predicted No-Effect Concentration
R_fD	Reference Dose
SF	Slope Factor
SPE	Society of Petroleum Engineers
STORET	Storage and Retrieval
TDS	Total Dissolved Solid
TSS	Total Suspended Solid
TOC	Total Organic Carbon
UF	Uncertainty Factor,

USA	United States of America
USDOC	United States Department of Commerce
USDOE	United States Department of Energy
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Carbons

Chapter 1

Introduction

1.1 Background of the study

Production of oil, to meet the world's energy demand, has increased by approximately 100% in each decade since the beginning of the 20^{th} century. Despite innovations in renewable energy technologies, the oil and gas sources are still supplying 63% of the world's total energy demand (Patin, 1999) and the other 37% of the total energy is from different sources of renewable energy including hydro, solar, wind, wave, wood and coal. In addition, the world's present population is increasing at an approximate rate of 76.5 million per year and consequently the industrialization demand is increasing. To cope with such increased demands, there is a quest to explore new oil and gas energy sources.

Exploration, development and production are the three main phases in oil and gas industry activities. During exploration, the oil reserve is estimated. Through drilling, process wells are constructed to extract oil and gas. During this phase, drilling cuttings and drilling muds are generated as wastes. In the production phase, the main wastes generated are produced water and produced sand. Produced water is the water brought up from the hydrocarbon bearing strata during the extraction of oil and/or gas. It includes formation water, injected water, small volumes of condensed water, and any chemicals added down hole or during the oil/water separation process (USEPA, 1993). Each year, 6.91 million m^3 of produced water is discharged to surface waters from the offshore industry (Wiedeman, 1996). The average discharge of produced water from one platform is about 1500 tonnes/day (GESAMP, 1993). Produced water can account for 2% to 98% of the extracted fluids from the reservoir (Stephenson, 1992; Wiedeman, 1996). Thus offshore oil and gas platforms became the largest source of oil discharges in the Norwegian sector of the North Sea in 1993, discharging 585 tonnes out of total 783 tonnes (Syvertsen et al. 1996).

The ratio between oil and water in produced water varies widely with time, location and properties of the formation layer. Over the economic life of a typical oil field, generation of produced water can exceed by ten times the volume of hydrocarbons (Stephenson, 1992). The ratio of oil to water in produced water for 30 oil and gas producing platforms has been estimated by the USEPA (1993) to be between 0.1 and 12.6. Since the produced water is the combination of water present in the hydrocarbon layers and process chemicals added to the hole during the production phase, its chemical composition is highly variable and complex in nature. 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. Despite their treatment, produced waters still contain toxic chemicals, which are of environmental concern. There is a concern that the produced water discharge may be causing contamination in fish and fish habitats (DFO, 2001). In the North Sea, sub lethal effects have been observed in both adult fish and larvae at varying distances from some platforms (DFO, 2001) discharging produced water.

The 5% to 10% concentration of typical produced water from a North Sea platform show 50% reduction in growth (EC_{50}) for *Photobacterium* and five other organisms (Brendehaug et al. 1992). The LC_{50} (Lethal concentration for 50% mortality) for Copepod (*Calanus finmarchicus*) based on a one-day exposure, as reported by Somerville et al. (1987), is 100 ml/l. Metal specific toxicological studies have been conducted in the past. For example, for an exposure duration varying from 8 days to 51 days, the LC_{50} and the maximum acceptable tissue concentration (*MATC*) of arsenic for saltwater crustaceans are in the range of 893 to 70000 μg/l, while the LC_{50} for fish, based on a 19-day exposure to cadmium, ranges from 108 to 16000 μg/l (ANWQG, 2000). A toxicological study for copper shows LC_{50} for molluscs (*Ostrea edulis*) based on a 5-day exposure as 20000 μg/l (ANWQG, 2000). Another study for effects of benzene on marine invertebrates (*Cancer magister*) determined LC_{50} based on a 40-day exposure in the range between 180 and 1200 μg/l (ANWQG, 2000). Since there are more than eighty distinct chemicals in produced water and their toxicity varies considerably, risk assessment studies for these chemicals is becoming an increasingly important issue (Ofjord et al. 1996).

Once the produced water is discharged into surface water, it is quickly diluted even within a 50m radius from the port of discharge (Furuholt, 1996; Meinhold et al. 1996; Mukhtasor, 2001). Numerous models (CORMIX, DREAM, OOC, CHARM) calculate dilution based on effluent and ambient properties. Ecological risk assessment studies from produced water were performed by Furuholt (1996), Stephens et al. (1996) and Karman et al. (1996) on the basis of contaminants in produced water. Meinhold et al. (1996) performed a human health risk study from radionuclides in produced water. Elevated levels of concentrations of contaminants in fish tissue were noted in several studies (Trefry et al. 1996).

The outfalls are designed on the basis of a 'Mixing Zone' concept, which is defined as the permitted impact zone where water quality criteria may be exceeded as long as acutely toxic conditions are prevented. Using the CORMIX (The Cornell Mixing Zone Expert System) model, which was developed by Doneker and Jirka (1990), the dilution of produced water can be predicted which indirectly gives the values of predicted environmental concentration (*PEC*). This software can designate a water quality criteria zone, which can be permitted as the mixing zone based on the regulations of different agencies. It does not, however, have any module to predict ecological or human health risk associated with the produced water. The software has not been designed as a tool to predict contamination from produced water discharges and does not have any database for produced water contaminants. The Dose Response Effects Assessment Model (DREAM), developed by Johnsen et al. (1999) does not have any module to predict human health risk. It predicts the effects to fish and zooplankton exposed to complex mixtures of chemicals (Johnsen et al. 1999).

The models discussed above are based on a deterministic approach. The types and quantities of chemicals in produced water are variable due to natural variability of reservoirs and differences in the process equipment used in separating the contaminants from produced water. In addition, ocean environmental variability and the model parameters' variability are important in calculating chemicals' concentration in marine biota. CORMIX and DREAM do not include the uncertainty due to the variability. For risk assessment purposes, the single-valued output may be an average value, which is one of the many different possibilities. Inclusion of the uncertainties in the model parameters and the concentration distributions would provide a better prediction of exposure concentration (*EC*) than those of the single value output models. The risk from produced water depends on the distribution of contaminants in the marine environment (Smith et al. 1996; Somerville et al. 1987; Karman and Reerink, 1997). The fish tissue concentration from a snap shot value of lipid content in a fish was predicted by the USEPA (1997); however the lipid content in fish is a seasonally variable factor (Campbell et al. 1988; Madenjian et al. 2000). The relevant uncertainty in lipid content needs to be incorporated for a more realistic prediction of the concentration of contaminants in fish tissues.

The effect of exposure period in predicting fish tissue concentration was ignored in the USEPA (1997) methodology. Change in fish weight within the exposure period has an effect on lipid, flesh and bone content. The edible part of a fish is determined as the summation of flesh, skin and lipid content. Metals and other chemicals are accumulated in the edible part of a fish and thus pose risk to human health through the food chain. Metals can be transported from tissue to tissue in the edible parts of the fish (Campbell et al. 1988). Metals can also bioaccumulate in fish liver and kidneys (Eisler, 2002). In addition to metals, naturally occurring radioactive materials (*NORM*) pose risks to human and marine life. Being chemically similar to calcium, the *NORM* components mostly accumulate in bones (Meinhold and Hamilton, 1992). Neff (2002) reported that more than 42 percent of the accumulated radium is deposited in the bone of a fish. Use of a uniform concentration throughout the whole body of a fish may lead to overestimation of risk from *NORM* components, as humans generally do not eat the bone/ shell/skeleton. Ratios of concentration factors for radium in non-edible parts to edible parts in a fish follow a lognormal distribution. The geometric mean of the ratios was predicted as 9.9. The total edible part of a fish varies from 64% to 87% (USEPA, 1996a).

There is no single general software that can be used for human and ecological risk assessment studies. There is also a need to fill the gap in the methodologies for human health risk assessment so that the risk to human health and ecological entities from contaminants in produced water can be predicted using a single software system. The integration of the produced water contaminants database with the available models and methodologies is also necessary to predict risk using a single software system. These issues are addressed in the present work.

1.2 Scope and purpose of the research

The proposed software in this research has the following features:

- Database for produced water contaminants; a total of 118 chemicals have been listed in the database. The chemicals are selected mostly from produced water from oil and gas platforms.
- Integrating the database of contaminants with initial dilution and subsequent dispersion models. Several dilution and dispersion models were studied before selection of the best models. The dilution model developed by Mukhtasor (2001) and the dispersion models by Doneker and Jirka (1990) and Huang et al. (1994) have been used in this study.
- Development of deterministic and probabilistic fish growth model. As discussed in the previous section, a fish growth model is a required component in this study. To incorporate the uncertainty, a probabilistic model has also been developed and integrated with the software system.
- Development of human health cancer and non-cancer risk assessment methodologies for non-radionuclides using probabilistic concepts.
- Development of human health cancer risk assessment methodologies for radionuclides using the concept of chemicals' distribution between bones/skeleton/shell and flesh in fish.
- Application of the methodologies to a hypothetical case study.

The database for produced water contaminants was developed through an extensive literature search with citation of references. All the references can be accessed and printed through the application. Chemical's physical, chemical and toxicological data for human, as well as marine species, including fish, have been stored in the database.

Navigation, addition of a new contaminant, printing and a query for data can be performed through user-friendly commands. Once the selection of contaminant(s) is done, the integration of contaminant(s) with the analysis is automatic. Both deterministic and probabilistic dilution models (Mukhtasor, 2001) have been integrated with dispersion models to characterize the exposure concentrations for marine biota. The input data fields have been arranged to make the analysis site-specific. The deterministic and probabilistic growth models for fish have been integrated with the exposure concentrations to predict fish tissue concentrations. The developed human health risk methodologies are integrated with the predicted fish tissue concentrations. Both deterministic and probabilistic approaches have been adopted in predicting human health cancer and non-cancer risk. The software predicts risk through individual chemicals for up to five non-radionuclide and three radionuclide contaminants. The total risk prediction is based on a probabilistic summation approach with a probabilistic concept of independence in occurrence of each event. The carcinogenicity is automatically detected through database properties. A case study is presented to highlight the application of the software.

1.3 Thesis outline

This thesis consists of seven chapters. The background, scope and purpose of the research are discussed in chapter 1. In chapter 2, the theoretical background of the research, the database for the chemicals associated with produced water, marine biota database and relevant properties are discussed. Chapter 3 presents the development of fish growth models. Chapter 4 covers the available dilution models, dispersion models, selection of initial dilution models, model parameters input, and fish growth model parameters.

In chapter 5, the framework for risk assessment is developed. The problem formulation, analysis and risk characterization for ecological risk assessment is discussed in this chapter. Prediction of exposure concentration for marine organisms, integration of fish growth models and prediction of contaminants' concentration in fish tissue are also discussed in chapter 5. Chapter 6 presents a hypothetical case study for an oil platform on the east coast of Canada. The developed models and methodologies for risk assessment have been applied in this case study based on the limited available data. Chapter 7 provides conclusions and recommendations for future studies.

Chapter 2

Characterization of Produced Water

2.1 Introduction

Offshore oil and gas fields have in the past been usually located in water depths up to 500 meters, which is known as the shelf zone. This is often also a zone of large-scale economic activities. A schematic of the shelf zone, which is bordered by the ocean coastline on one side and by the continental slope on the other side, and exceeds 30 million square kilometers in the world, is presented in Figure 2.1. Oil and gas reservoirs have a natural water layer known as formation water. The water that lies under the hydrocarbon layers in the reservoirs is the main source of chemicals in produced water (Figure 2.2). Most of the offshore oilfields produce large quantities of contaminated water that can have significant environmental effects when discharged, if not handled properly. Produced water is the highest volume waste generated during oil and gas production operations. The quantity of produced water from an oil field varies from site to site depending upon the characteristics of the oil reservoir and the age of the field.

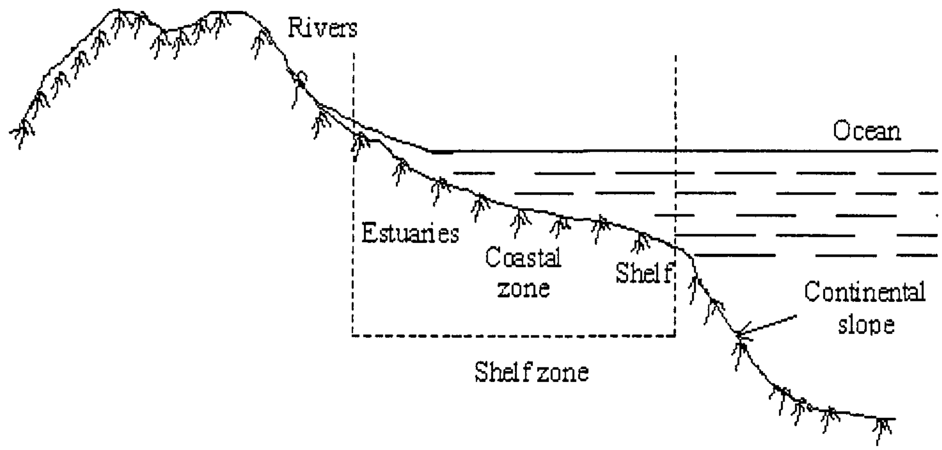


Figure 2.1 Typical shelf zone (modified after Patin, 1999)

The amount of treated produced water discharged from a single platform is usually less than 1500 m^3 per day whereas discharge from large treatment facilities that process produced water from several platforms may be as high as 25,000 m^3 per day (Menzie, 1982). In the year 1990, the oilfields of the Gulf of Mexico (GOM) produced 5.45 million m^3 of water (Reilly, 1991) while the oil fields in the UK sector of the North Sea discharged 148 million m^3 of produced water into the sea in 1993 (HMSO, 1994). Discharge of produced water on the UK continental shelf from 1991 to 2000 is presented in Figure 2.3. In this sector, produced water discharge was increased by 60% from 1991 to 2000. The oil discharged into the North Sea with the produced water from the UK sector varies in the range of 0.0038% to 0.0066% of the total oil produced in this sector. In the period from 1995 to 2000, the discharged oil was almost 0.005% of the total produced oil in this sector. Produced waters are treated to satisfy regulatory standards before being discharged into the sea. In the UK sector of the North Sea, the oil content in discharged produced water shows a decreasing trend as shown in Figure 2.4. But the amount of produced water discharge has an increasing trend (Figure 2.3). As a result, the total amount of oil discharged into the ocean remains approximately the same from 1991 to 2000 in this sector (Figure 2.3).

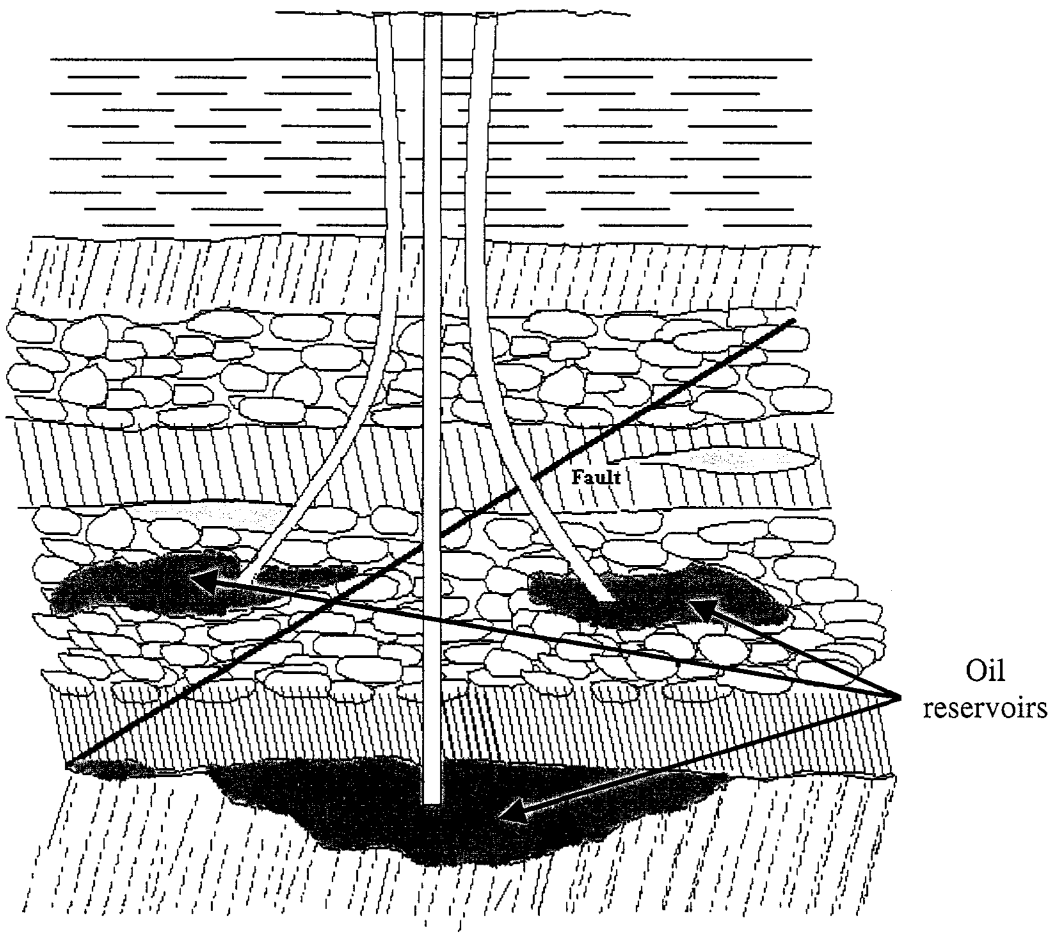


Figure 2.2 Typical location of oil and gas reserve (modified after Patin, 1999)

In the Norwegian sector of the North Sea, a similar increase of produced water discharge (above 90 million tonnes) and associated oil is expected (Brandehaug et al., 1992). The rate of discharge varies from 4000 m^3/day in the Gulf of Mexico, USA, to 123000 m^3/day in the Java Sea, Indonesia (Brandsma and Smith, 1996; Smith et al., 1996; Somerville et al. 1987). An average discharge from a coastal well ranges from 1.7 m^3 per day in the Gulf coast to 7.4 m^3 per day in Cook Inlet, Alaska (Wiedeman, 1996). In each year, approximately 1.4 million m^3 of produced water is discharged to surface waters by the coastal oil and gas industry (Wiedeman, 1996). The Offshore Operators Committee (OOC) conducted a study of 42 platforms in the Gulf of Mexico that discharged 419 m^3 of oil into the Gulf of Mexico in 1989 while in the same year, 4119 m^3 of oil was discharged into the North Sea from 89 platforms (Stephenson, 1992).

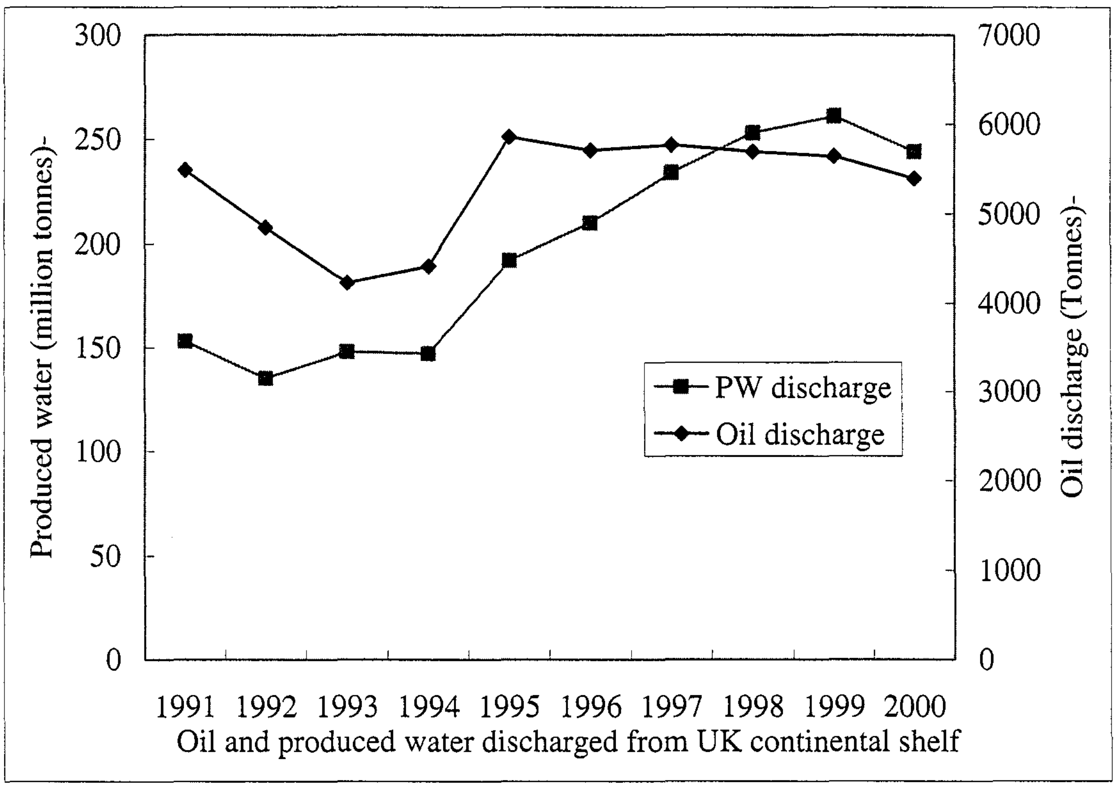


Figure 2.3 Oil and produced water discharges on the UK Continental Shelf (data source: Development of UK Oil and Gas Resources 2001; http://www.dbd-data.co.uk/bb2001/contents.htm)

The Oslo and Paris (OSPAR) commission predicted the increased discharge of oil from produced water in the North-East Atlantic area since 1984 (Wills, 2000) as a result of increased amount of produced water discharge. The volume of treated produced water discharged into the ocean in different parts of the world is presented in Table 2.1. Despite regulatory limitations on oil concentrations in the discharged produced water, the total amount of discharged oil is increasing throughout the world, which is mainly due to the increased amount of produced water discharge. The average discharges in the different regions are not the same as shown in Table 2.1. The Gulf of Mexico has the highest rate of produced water discharge (Table 2.1) to the sea.

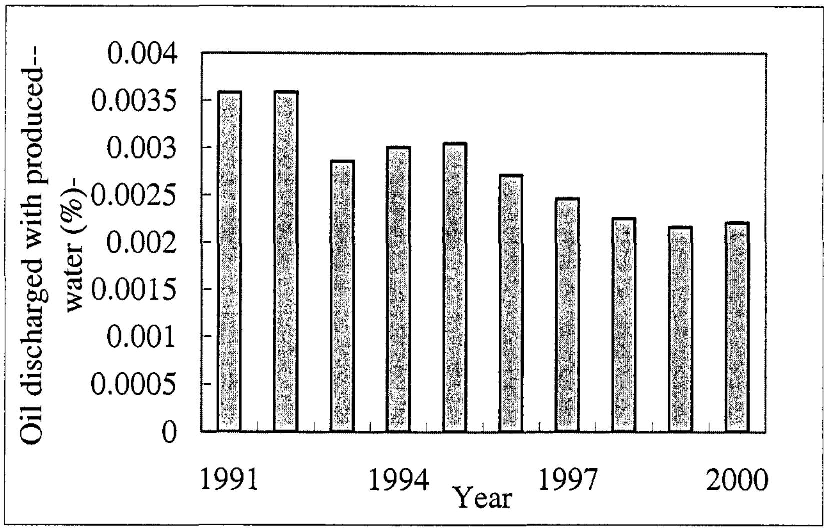


Figure 2.4 Oil as a percent of produced water on the UK Continental Shelf (Data source: Development of UK Oil and Gas Resources 2001; http://www.dbd-data.co.uk/bb2001/contents.htm)

Table 2.1 Volume of produced water discharged into ocean (source: Neff, 1998)

Location	Discharge rate (m^3/day)
US Gulf of Mexico	549000
Offshore, California	14650
Cook Inlet, Alaska	22065
North Sea	512000
Australia	100000
West Java Sea (3 offshore facilities)	192000

2.2 Oil to water ratio in produced water

The ratio between oil and produced water varies widely with time, location and properties of the formation layers. In the early stages of production, the volume of produced water is relatively small, but with time, the hydrocarbon yield decreases and the produced water volume increases (Wiedeman, 1996). As a consequence of hydrocarbon layer depletion, injection of more water into the well is required to maintain the pressure for oil and gas extraction and it results in more produced water generation over the economic life. Table 2.2 shows the ratio of oil to produced water from 30 platforms. Some statistics of the ratios are: maximum 12.63, minimum 0.1, mean 3.5 and median 1.7 (USEPA, 1993).

2.3 Physical properties of produced water

Physical properties of produced water depend on characteristics of the formation water layer, type of oil or gas produced (e.g. heavy or light), types and quantities of contaminants and treatment followed during production. Table 2.3 represents the variability in the physical properties with locations and quantities discharged into the sea. The discharge of produced water to the sea from individual platforms is in the range of 314 - 2.4×10^5 m^3/day and the density of produced water varies between 988 - 1185 kg/m^3 (Table 2.3). Oil concentration in the discharged produced water ranges between 2 - 565 mg/l and the pH ranges from 3.7 to 10. Produced water also contains dissolved and suspended solids and some produced water has higher salinity level (Table 2.3).

Table 2.2 Oil to water ratio in produced water. (source: USEPA, 1993)

Company	Platform	Oil/Condensate (bbl/day)	Produced water (bbl/day)	Water to oil ratio
Conoco	EC 33A	76.6	62	0.81
Mobil	EC 14CF	807	2005	2.48
Conoco	V 119D	890	2817	3.17
Shell	V 255A	950	1298	1.37
Gulf	SMI 23B	228	495	2.17
Shell	V 39D	395	634	1.61
Exxon	SMI 6A	250	625	2.5
Marathon	EI 57A-E	1200	500-2000	0.42-1.67
Shell	SMI 115A	750	1200	1.6
Mobil	EI 120CF	3500	2000	0.57
Shell	SMI 130B	21500	9733	0.45
Conoco	EI 208B	1501	350	0.23
Shell	EI 18CF	2000	22000	11
Gulf	EI 238A	40	2	0.05
Placid	EI 296B	1500	1470	0.98
Chevron	SS107 (S94)	501	4610	9.2
Chevron	SS107 (S93)	2875	12500	4.35
Amoco	SS 219A	3000	800-1000	0.27-0.33
Gulf	ST 177	2800	1072	0.38
Shell	BM 2C	10794	6590	0.61
Texaco	BDC CF5	873	11028	12.63
Gulf	ST 135	6000	8400	1.4
Amoco	WD 90A	2244	15000	6.68
Conoco	WD 45E	745	1578	2.12
Conoco	WD 70I	5273	10721	2.03
Texaco	GIB DB600	554	3796	6.85
Shell	WD 105C	2091	7532	3.60
Shell	SP 62A	1800	3100	1.72
Shell	SP 24/27	24000	150000	6.25
Shell	SP 65B	5000	3000	0.6

Table 2.3 Physical properties of produced water

Platform Details	Oil Produced (m^3/day)	PW Discharge (m^3/day)	Seawater density (kg/m^3)	PW density (kg/m^3)	Oil content (mg/l)	Temperature (^0C)	Salinity (mg/l)	pH	DO (mg/l)	COD (mg/l)	TOC (mg/l)	TSS (mg/l)	TDS (mg/l)
Magnus (18 fields), North Sea[a]	79493.65	37750-106000	1025	1020	8.0-360	59-68	17-1800	-			140-160		
Forties Delta[a]		239000		1049	68	76	44400				340		
Ula[a]		81760		1048	37	68	40440				71		
Cleeton[a]		314		1000	58	14.3	31				290		
Clyde[a]		314500		1080	34	72	72700				45		
Forties Charlie[a]		201300		1040	50	76	34200				250		
North Sea Platforms		70-1573300		------	2-220	na	44630				na		
Brent[b]	10800	17222		1018	7.8	40	24000						
Brae[b]	3791	4335		1039	68	69	30000						
Forties[b]	4284	8583		1039	50	76	34000						
Clyde[b]	4134	9062		1080	40	72	71000						
Roswell[c]							122450	6.8-7.2	0.1		250	25000	225000
Hobbs[c]							34000	6.8-7.4	0.06		155	200	59800
Lovington[c]							1198	7.0-7.3	1.4		694	400	5700
North Sea[d]				1014-1185	2.0-64		12400-81000	6.7-7.3		nc	100-1000	-----	
Murchison[d]				1020-1021	7.0-75		16900-18690	7.1-8.1		441-869	142-335	15-85	
Hutton[d]				1019-1025	9-220		10310-21035	6.9-8.3		127-2070	15-522	3.0-29.0	
World[d]				1014-1140	2-565		80-200000	4.3-10		1220	0-1500	1.2-1000	
Kepple Creek (KC1)[e]		2690.6-110070				2.0-28		5.0-7.1	6.7-13.9				13-430
Kepple Creek (KC2)[e]		0.0-41582				3.5-25		5.1-6.7	1.9-13.1				20-156

Platform Details	Oil Produced (m^3/day)	PW Discharge (m^3/day)	Seawater density (kg/m^3)	PW density (kg/m^3)	Oil content (mg/l)	Temperature (^0C)	Salinity (mg/l)	pH	DO (mg/l)	COD (mg/l)	TOC (mg/l)	TSS (mg/l)	TDS (mg/l)
Little Hurricane Creek (LHC2)[e]		2935.2-259276				4.0-26		5.1-7.1	7.1-13				14-90
Little Hurricae Creek (LHC3)[e]		1687.74-264168				1-25.5		5.1-6.8	6.5-13.2				23-90
Hurricane Creek(HC2)[e]		22014-670204				6.5-13.2		3.8-6.3	6.2-12.5				44-368
Hurricane Creek(HC3)[e]		17855.4-562580				6.2-12.5		3.7-6.2	6.2-12.5				58-388
Hurricane Creek(HC4)[e]		1149.6-210356				6.4-13.1		5.1-7.4	5.1-7.4				14-91
Bass Strait[f]		14000	1026	988		90							
Gulf of Mexico[f]		3977.8	1017	1088		29							
Java Sea[f]		26235-123225	-----	----		62-90							
North Sea[f]		10000	1027	1014		30							
Bintulu COT[g]							12000	8.2	2.15			58	
Lutong COT[g]							16000	8.5	1.45			137	
Labuan COT[g]							17000	8.8	1.4			706	
Murchison[d]				1020-1021	7.0-75		16900-18690	7.1-8.1		441-869	142-335	15-85	

a. Flynn et al. (1996) c. Tellez and Nirmalakhandan (1992) e. O, Neil et al. (1992)
b. Stagg et al. (1996) d. Tibbetts et al.(1992) f. Smith et al. (1996), Somerville et al. (1987), Brandsma and Smith (1996) g. Din et al. (1992)

2.4 Contaminants in produced water

As produced water is the mixture of formation water, injected water, chemicals added during extraction of oil and gas and the process chemicals used to treat the produced water, it may contain toxic chemicals that are of concern for the marine environment. The contaminants in produced water can be categorized into metals, *BTEX* (Benzene, Toluene, Ethyl Benzene and Xylenes), *PAHs* (polycyclic aromatic hydrocarbons), *NPD* (Naphthalene, Phenanthrene and Dibenzothiophene including their alkyl homologues) and *NORM* (naturally occurring radioactive materials).

The toxicity and persistence of *PAHs* in produced water is of the greatest environmental concern (Neff, 2002) and thus led to many studies associated with their effects (OGP, 2002; Neff and Sauer, 1996; Mulino et al. 1996). The metals that are present most frequently in produced water are Barium, Cadmium, Chromium, Copper, Iron, Nickel, Lead and Zinc (Neff, 2002). Because of their bioaccumulative nature, the metals may pose risk to the marine environment (Trefry et al. 1996). Despite the high amounts of *BTEX* in produced water, the *BTEX* may not pose high risk as these compounds evaporate rapidly as soon as they are discharged into the marine environment (Furuholt, 1996). As *NORM* components in produced water have long half-lives, they may pose risk to human health through the food chain. Meinhold et al. (1996) performed human health cancer risk studies from radionuclides in produced water.

Dissolved aliphatic hydrocarbons (Decane through Tetratriacontane) in produced water from paraffinic oils are within the range of 606-2677 μg/l (OOC, 1975; Lysyj, 1981; OOC, 1982; Burns, 1983; Middleditch, 1983; Caudle, 1988; Brown, 1990).

Phenols have been found in varying amounts in the water associated with all types of oils (Paraffinic, Asphaltenic, Gas condensate). The water from gas condensate has a higher quantity of phenols and low molecular weight aromatic compounds (Callaghan, 1990). Produced water from paraffinic oils generally has a higher concentration of simple fatty acids but produced water from asphaltenic oils can have notable amounts of naphthenic acids (Stephenson, 1992). Treatment of produced water is applied on the platform under a certain set of rules before discharge into the ocean. This water still contains some oil and/or residues. The contaminants' type and concentration vary from well to well, even among the different layers in the same well (Patin, 1999). The difference in the lower limit and upper limit of various types of contaminants and their diffusion characteristics in ambient seawater make the environmental impact assessment complex.

The worldwide petroleum hydrocarbon input into the oceans from produced water represents about 0.4% of the total amount of petroleum hydrocarbons entering the world's oceans from all sources (NRC, 1985). Petroleum hydrocarbons usually represent 10% to 65% of the total organic matter in the produced water (Neff et al. 1996). The organic chemicals, heavy metals and radionuclides in produced water are of concern for ecology and human health and therefore a considerable volume of literature addressing effects of produced water discharges has been developed (Ray and Engelhardt, 1992; Reed and Johnsen, 1996).

Roe et al. (1996), Smith et al. (1996) and Stephenson, (1992) studied several oil development platforms for contaminants in the North Sea, Gulf of Mexico, Java Sea and Bass Straits. Their findings are tabulated in Table 2.4. The average concentrations of metals in North Sea produced water are much higher than those of the Gulf of Mexico or the Java Sea, while the average concentrations of *BTX*, *NPD*, *NORM* and *PAHs* are higher in the Gulf of Mexico than those of the North Sea produced water. Radionuclides are highest in the Gulf of Mexico (Neff, 2002; Stephenson, 1992). The ranges of concentrations for organic chemicals and metals in produced water worldwide vary significantly. The information compiled after Neff et al. (2002) is presented in Table 2.5.

Table 2.4 Typical concentrations of different pollutants in different regions (Units are in μg/l otherwise stated; Data compiled from Roe et al. (1996), Smith et al. (1996), Stephenson (1992), Stagg et al. (1996) and Neff (2002))

Parameter	North sea (6 platforms)			Gulf of Mexico			Java Sea (6 platforms)			Bass Straits
	Min	Ave	Max	Min	Ave	Max	Min	Ave	Max	
As	nr	nr	nr	nr	nr	nr	1.5	4.7	9	<1.5
Ba	12000	27430	42100	nr	nr	nr	nr	nr	nr	nr
Cd	20	6670	10000	0	27	98	nd	0.5	nd	<5
Cr	0.05	13.2	40	0	186	390	7.5	124	185	<5
Cu	2	128.8	600	0	104	1455	nd	5.2	nd	<5
Fe	4	20.57	23	nr	nr	nr	nr	nr	nr	nr
Hg	1.9	4	9	nr	nr	nr	0.004	0.006	0.0012	0.044
Ni	nr	nr	nr	0	192	1674	45	95	143	<5
Pb	50	112.5	270	2	670	5700	12	193	260	23
Zn	0.26	47	200	17	170	1600	nd	nd	nd	<30
Benzene	1417	4430	6853	2	1318	8722	69.3	1720	3000	24
Toluene	2174	2571	2947	60	1065	4902	90.8	650	1300	nr
Ethylbenzene	425	961	1503	26	68	110	26	41	56	
Xylene	675	2201	3411	160	440	720	13	247	480	
BTX	1100	15740	66900	nr	nr	nr	nr	nr	nr	nr
Naphthalene	38	272	398	0	132	1179	8.4	35	99	1.6
Phenol	33	1934	5100	0	1049	3660	nr	nr	nt	nr
^{226}Ra (pCi/l)	nr	nr	nr	4	262	584	nr	nr	nr	nr
^{228}Ra (pCi/l)	nr	nr	nr	18	277	586	nr	nr	nr	nr

Note nr: data were not reported; nd: data were not detected; Min: Minimum; Ave: Average; Max: Maximum

The contaminants in produced water are generally a large number of organic and inorganic chemicals that are dissolved and dispersed into the produced water from the geological formation layers over millions of years. There is a concern about the aromatic substances in produced waters. These are mainly a diverse group of unsaturated cyclic compounds principally of carbon and hydrogen. Some heteroatoms may also be present in produced water (OGP, 2002). The bulk composition of aromatic hydrocarbons in produced water does not vary significantly over the life of a field and there appears to be poor relationship between total oil content and the concentration of aromatic compounds (OGP, 2002). The concentration of aromatic compounds in produced water from 18 oil production fields operated by Norsk Hydro and Statoil in the Norwegian sector of the North Sea is presented in Table 2.6.

Table 2.5 Organic chemicals, radium and metals in produced water

Parameter	Concentration (μg/l)
Total Organic Carbon (TOC)	≤ 100 - ≥11000000
Total Saturated Hydrocarbons	17000-30000
Total Benzene, Toluene, Ethylbenzene, Xylenes (BTEX)	68-578000
Total Polycyclic Aromatic Hydrocarbons (PAHs)	40-3000
Steranes /Triterpanes	140-175
Total Phenols	600-23000
Organic Acids	≤ 1-10000000
Sulfates	≤ 1000-8000000
Arsenic	0.004-320
Barium	<1.0-2000000
Cadmium	0.0005-490
Chromium	<0.001-390
Copper	<0.001-55000
Lead	<0.001-18000
Manganese	0.2-7000
Mercury	<0.001-75
Nickel	<0.001-1670
Iron	0.1-465000
Zinc	0.005-200000
Total Radium (pCi/l)	0-5150

The *PAHs* assemblage is dominated by the more soluble lower molecular weight two and three-ring *PAHs*. Alkyl *PAHs* are more abundant than the parent compounds and phenanthrene is more abundant than anthracene (Neff, 1979). The aromatic fraction of produced water is dominated by *BTEX* and *NPD* (OGP, 2002). These compounds are highly soluble in water. High molecular weight *PAHs* are less water-soluble (Neff et al. 1996) and thereby less harmful to marine species. They are present mainly in or associated with dispersed oil (OGP, 2002). Moreover, the higher molecular weight *PAHs* are mostly removed from produced water before discharge and thus the impacts induced by the higher molecular weight *PAHs* are reduced. The solubility of petroleum hydrocarbons in seawater decreases as their size (molecular weight) increases (Eastcott et al.1988; McAuliffe et al. 1966). The efficiency of dispersed oil separation has very little impact on the more soluble lower molecular weight *PAHs*. Thus the only *PAHs* from produced water that can reach lethal concentrations in receiving waters are the two and three- ring *PAHs*. The *BTEX* compounds are volatile and will evaporate rapidly from produced water discharged close to the sea surface or from the positively buoyant plumes. The *NPD* components are less volatile but will evaporate to some degree. The *PAHs* compounds are the less water-soluble compounds and are expected to be associated with particulates and oil droplets in the produced water (OGP, 2002).

As the produced waters are subjected to treatment prior to discharge into the sea, the concentrations of the contaminants in the treated produced waters are of interest. The regulatory limitations of permissible oil content in produced water are different in different regions.

Table 2.6 Concentration of aromatic compounds in produced water (source: OGP, 2002)

Compound	Minimum concentration (μg/l)	Maximum concentration (μg/l)
Benzene	32	14966
Toluene	58	5855
Ethyl benzene	86	565
M- Xylene	258	1289
P-Xylene	74	331
O- Xylene	221	1064
Total BTEX	**730**	**24070**
Naphthalene	194	841
C1-Naphthalenes	309	2901
C2-Naphthalenes	145	3207
C3-Naphthalenes	56	2082
Phenanthrene	9	111
C1- Phenanthrenes	17	323
C2- Phenanthrenes	14	365
C3- Phenanthrenes	9	273
Dibenzothiophene	1	23
C1- Dibenzothiophenes	6	103
C2- Dibenzothiophenes	4	120
C3- Dibenzothiophenes	3	89
Total NPD	**766**	**10439**
Acenapthylene	0.1	6.1
Acenapthene	0.3	15.3
Fluorene	4.1	66.7
Anthracene	0.1	2.6
Fluoranthene	0.1	3.6
Pyrene	0.2	7.7
Benz (a) anthracene	0.1	2.8
Chrysene	0.6	15.2
Benzo (b) fluoranthene	0.1	3.4
Benzo (k) fluoranthene	0.0	0.6
Benzo (a) pyrene	0.0	1.1
Indeno (1,2,3 –c, d) pyrene	0.0	0.4
Dibenz (a, h) anthracene	0.0	1.2
Benzo (g, h, i) perylene	0.0	2.7
Total 16 EPA PAHs	**5.8**	**129.2**

The regulatory limitations of oil content with discharged produced water for different regions are presented in Table 2.7. The regulations allow the discharge of oil up to a certain level and thereby the dispersed contaminants as well as the dissolved contaminants are discharged into the sea with the produced waters. The water-soluble fraction of produced waters consists of a large variety of polar organic compounds originating from the oil itself, formation waters in the reservoir and the chemicals in the production process (Brendehaug et al, 1992). Contaminants in BPT (Best practicable technology) treated produced water are presented in Table 2.8.

Table 2.7. The regulatory limitations in different regions

The OSPAR area	Discharged oil to produced water ratio must not exceed 40 ml/l. OSPAR plans to reduce it to 30 ml/l by 2006.
The North Sea (UK Sector)	UK sector North Sea discharge limitation 35 ml/l
Norway	Discharged oil to produced water ratio must not exceed 40 ml/l. (Regulation imposed by State Pollutant Control Authority (SFT))
Canada	30 day average: 40 ml/l; 24 hour average: 60 ml/l. (C-NOPB 2001, NEB)
United States	30 day average: 29 ml/l; 24 hour average: 42 ml/l. (US EPA, MMS (Minerals Management Service).

Table 2.8 Pollutant concentrations for best practicable technology (BPT) treated produced water Effluent (source: Wiedeman, 1996)

Pollutant	Settling effluent concentration (μg/l)	Pollutant	Settling effluent concentration (μg/l)
Conventional and non-conventional pollutants		Trichlorofluoromethane	294
Total Recoverable Oil and Grease	53×10^3	Other Volatile Organics	
Total suspended solids	0.13×10^6	Carbon Disulphide	8.48
Ammonia	65.8×10^3	Chloromethane	28.6
Chlorides	65.1×10^6	m- Xylene	136
Total Dissolved Solids	84.04×10^6	O &P Xylene	86.1
Total Phenols	2030	Vinyl Acetate	29.4
Priority Pollutants Metals		2-Butanone	122
Antimony	166	2- Hexanone	35.8
Arsenic	10.80	2- Propanone	913
Beryllium	5056	Priority Pollutants (Semi volatile organics)	
Cadmium	22.80	Bis (2-Ethylhexl) phthalate	46
Chromium	128	Di-N- Butyl Phthalate	46
Copper	180	Naphthalene	144
Lead	515	Phenol	553
Mercury	0.58	Other Semi volatile organics	
Nickel	109	Benzoic Acid	3813
Selenium	250	Benzyl Alcohol	49.5
Silver	252	Hexanoic Acid	790
Thallium	180	n- Decane	139
Zinc	329	n- Docosane	38
Other Metals		n- Dodecane	225
Aluminium	1072	n-Eicosane	68
Barium	52573	n-Hexosane	36.1
Boron	20244	n-Hexadecane	283
Calcium	2.5×10^6	n-Octacosane	35.2
Cobalt	83.6	n-Octadecane	82.9
Iron	15492	n-Tetracosane	38.2
Magnesium	615.7×10^3	n-Tetradecane	119
Manganese	1301	n-Triacontane	35
Molybdenum	86.9	o-Cresol	121
Strontium	205.5×10^6	p-Cresol	149
Sulfur	96830	1, 2: 3, 4 Di epoxy butane	71.1
Tin	305	2-Methylnapthalene	67.2
Titanium	32.4	2-4 Dimethylphenol	117
Vanadium	96.6	Radionuclides (pCi/l)	
Yttrium	25	Gross alpha	383.54
Priority Pollutants (Volatile Organics)		Gross Beta	312.63
Benzene	4285	Lead 210	64.28
Ethylbenzene	115	Radium 226	172.18
Methylene Chloride	170	Radium 228	228.4
Toluene	3370		

2.5 Database

Removal of contaminants from produced waters follows several standard procedures. Characterization of produced water has been conducted by several studies including Brendehaug et al. 1992; Tibbetts et al. 1992 and Shepherd et al. 1992. Physical and chemical properties of different chemicals have been extensively studied through numerous studies (Howard et al. (1979-1991); Mackay et al. (84-2001); Mackay and Shiu, and others). Studies on the lethal effects to marine fish and other invertebrates from produced water components have become important to environmental engineers and ecological scientists.

Despite numerous studies on produced water contaminants, their fate and transport in the marine environment, toxicity, discharge concentrations and risk induced to the ecology and humans, the data of produced water contaminants for risk assessment purposes is not well organized. Organization of the toxicological information and other related physical and chemical properties for the contaminants in produced water are necessary to make the data available for risk assessment studies.

2.5.1 Produced water contaminants database

A database on contaminants, consisting of physical, chemical and toxicological information was assembled in this research. Some process chemicals that are added in several steps of the production process have also been included. A collection of 118 contaminants has been organized in the database. The database can be expanded through a simple procedure. The properties included in the database are discussed briefly below.

- **CASRN:** Each chemical has a unique number for identification. This number is termed as 'Chemical Abstracts Service Registry Number'. For example, the *CASRN* of benzene is 71-43-2 and toluene is 108-88-3.
- **Molecular Weight:** The molecular weight of any compound (g/mol) is the mass per gram mole. For example, water has a molecular weight of 18.01 whereas the molecular weight of Toluene is 92.13.
- **Henry's Law Constant (*HLC*):** The pressure of the gas above a solution is proportional to the concentration of the gas in the solution (Pa-m^3/mol). For example, Acetic acid has a Henry's law constant of 0.0182 Pa-m^3/mole.
- **Toxicity Weighting Factor (*TWF*):** Ratio of potential effects of a chemical to the effects from an equal amount of copper (standard chemical for developing weighting factors by USEPA, 1993). For example, Arsenic has a toxicity-weighting factor of 4.16 while for Antimony it is 0.0125.
- **Carcinogenicity:** A chemical that poses a risk of cancer is classified as a carcinogen. The USEPA (1984) classified the chemicals according to the weight of evidence.

A: Human carcinogen (known human carcinogen)

B: Probable human carcinogen. These are grouped into two subcategories as B_1 for limited human evidence and B_2 for sufficient evidence to animals and inadequate or no evidence in human.

C: Possible human carcinogen.

D: Not classified as to human carcinogenicity.

E: No evidence of carcinogenicity in humans or evidence for non- carcinogenicity for humans. For example, benzene is a carcinogen but chromium is not.

- **Slope Factor (*SF*):** The slope factor for a chemical relates the chronic dose to the lifetime risk. *Slope factor = risk / unit dose*. Slope factor is used only for carcinogenic chemicals. Benzo[a]pyrene has a slope factor of 0.00033 $(mg/kg/day)^{-1}$

- **Reference Dose (R_fD):** Maximum dose of the chemical that will not cause any harmful effect (mg/kg-day) to humans. It is used for non-carcinogenic chemicals or for those that have both carcinogenic and non-carcinogenic characteristics. Cadmium has R_fD = 0.0005 (mg/kg/day). The reference dose is defined as an estimate of a daily dose for which no risk of deleterious effects during a lifetime is expected.

- **Suspended Solid-Water Partition Coefficient (*Kssdw*):** The ratio of concentration of pollutant in the suspended solids to the concentration in water at equilibrium is the suspended solid-water partition coefficient. Cadmium has a partition coefficient of 320000 to suspended solid.

- **Bioconcentration Factor (*BCF*):** The ratio between the concentration of a chemical in an organ or organism to the concentration in water. The bioconcentration factor can vary from species to species. For example, cadmium has a bioconcentration factor of 2213 l/kg for fish.

- **Vapor Pressure:** The particle pressure of a vapor at the surface of its parent liquid at 25°C. For example, Water has a vapor pressure of 101 kPa, whereas benzene's is 12.7 kPa.
- **Solubility:** The solubility of the compound in water at 25°C. For example, benzene has a solubility of 0.0018 mg/L.
- **Conversion Factor (*CF*):** In the toxicity test, some fraction of metal is dissolved and some is bound to particulate matter. The dissolved fraction of metals closely approximates the biologically available fraction. The conversion factors predict how different the criteria would be if they have been based on measurements of the dissolved concentrations. Each metals total recoverable fraction must be multiplied by the conversion factor to obtain a dissolved criterion that must not be exceeded in the water column. For example, at a water hardness of 100 mg/l as $CaCO_3$, the acute total recoverable criterion for silver is 4.06 μg/l. The conversion factor for silver is 0.85. So the dissolved silver criterion is 3.45 μg/l. The conversion factor for Cadmium is 0.994 (USEPA, 1996).
- **Sorption Coefficient (K_{oc}):** The sorption constant is defined in two ways: the adsorption of the compound on organic carbon and the distribution of the compound in the soil. For example, benzene has a K_{oc} of 1.74.
- **Octanol-Water partition coefficient (K_{ow}):** is defined as the ratio of a chemical's concentration in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system. For example, Benzene has Log (K_{ow}) = 2.13.

- **Half Life ($T_{1/2}$):** The time required to reduce the amount of chemical by half. According to a first order decay reaction, the half-life of a chemical is defined by $0.693/k$ where k is the decay rate of the chemical in the media. For example, Benzene has a half life of 170 hours in water.
- **Leaching Factor (*LF*):** The fraction of a chemical that is leached into the media. In this case, the medium is water. For example, Barium has a leaching factor = 0.0021.
- **Uncertainty Factor (*UF*):** Dose extrapolations for humans from animal studies are associated with several uncertainties. Several categories of uncertainties are assigned to quantitative risk assessment. The uncertainty factors are calculated as $F_1 \cdot F_2 \cdot F_3 \cdots\cdot F_n$ where F_1, $F_2 \cdots F_n$ are the uncertainties from various sources. If animal studies data are used for dose calculation the uncertainty is $UF=10\times10\times10=1000$ (10 for interspecies, 10 for intraspecies, 10 for potential synergism). When the exposure pathway is inappropriate, another factor will have to be incorporated and the total uncertainty would become 10000. If the data were collected from a human study then interspecies variation would become 1 and the UF would be 100 (Hallenbeck and Cunningham, 1991).
- **Lowest Observed Adverse Effect Limit (*LOAEL*):** The lowest concentration of a chemical for which an effect is observed. For Barium, *LOAEL* to fish is 0.21 μg/l.

- **No Observed Adverse Effect Limit (*NOAEL*):** No observed adverse effect limit: The concentration of a chemical that does not show any adverse effect to the exposed animal.
- **No Observed Effect Concentration (*NOEC*):** It is the highest dose of a chemical to any organism for which no effect is observed. For example, Cadmium has a *NOEC* of 2.53 μg/l for fish.
- **Typical concentration in the Ocean:** The background level of cadmium in the ocean is 0.02 μg/l.
- **Lethal Concentration for 50% Mortality (LC_{50}):** The lethal concentration at which 50% of the exposed organisms died. Cadmium has LC_{50} for a fish of 2.95 μg/l.
- **Sediment-Water Partition Coefficient (*Ksedw*):** The ratio of concentration of pollutant in the sediment to the concentration in water at equilibrium, Cadmium has a partition coefficient of 2000 for sediment.

The interface of the database is presented in Figure 2.5. Data for all contaminants can be accessed directly from the database window. It is presented in Figure 2.6. The specific reference can be viewed by double clicking the relevant reference number. It is presented in Figure 2.7. The particular definition can be viewed through clicking on the property name. Figure 2.8 shows the related interface.

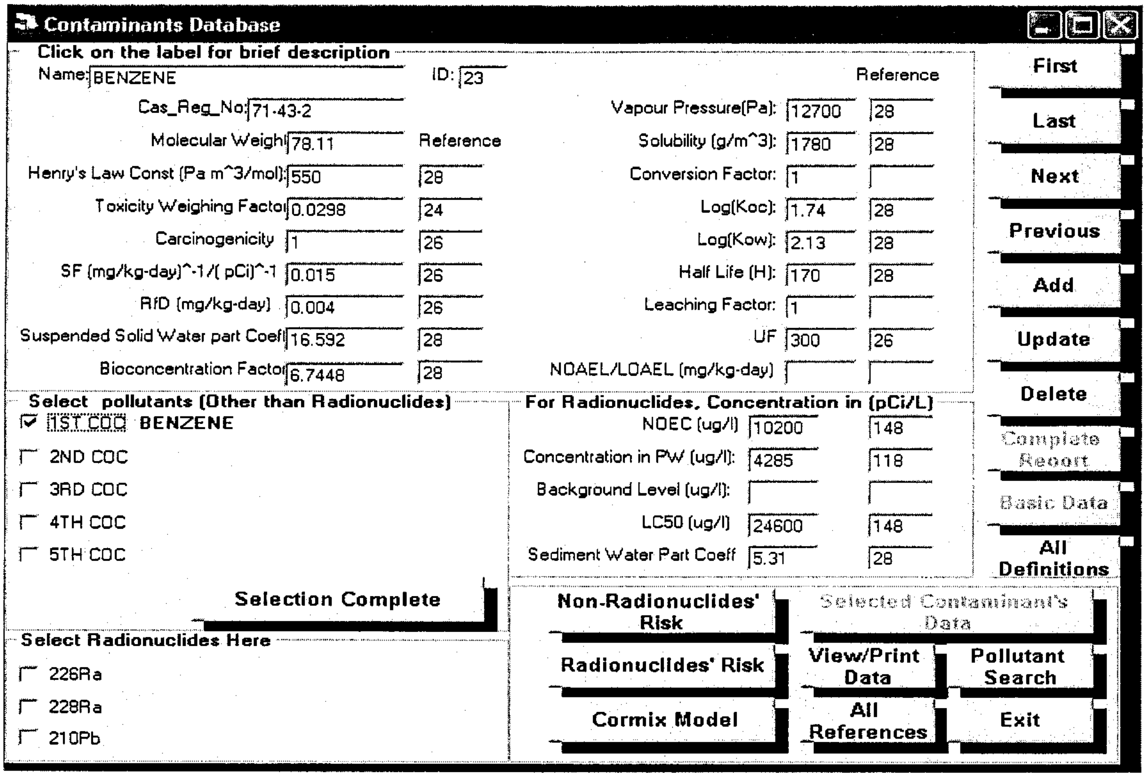
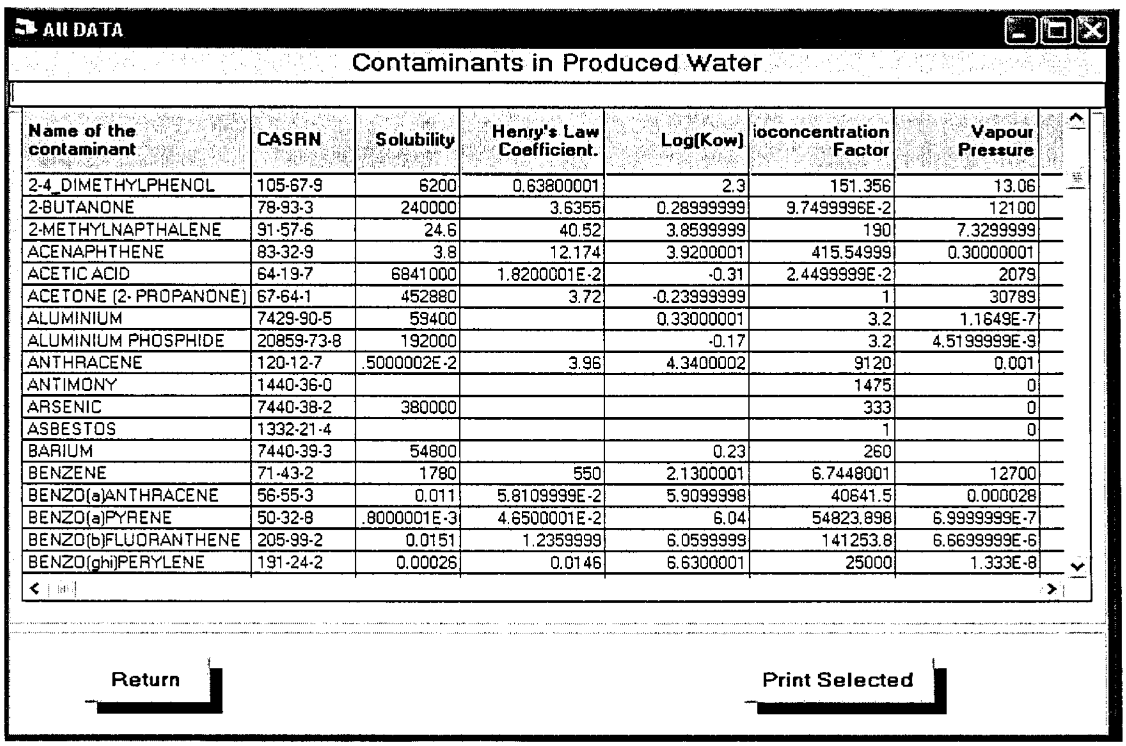


Figure 2.5 Contaminants' database form



Name of the contaminant	CASRN	Solubility	Henry's Law Coefficient.	Log(Kow)	ioconcentration Factor	Vapour Pressure
2-4_DIMETHYLPHENOL	105-67-9	6200	0.63800001	2.3	151.356	13.06
2-BUTANONE	78-93-3	240000	3.6355	0.28999999	9.7499996E-2	12100
2-METHYLNAPTHALENE	91-57-6	24.6	40.52	3.8599999	190	7.3299999
ACENAPHTHENE	83-32-9	3.8	12.174	3.9200001	415.54999	0.30000001
ACETIC ACID	64-19-7	6841000	1.8200001E-2	-0.31	2.4499999E-2	2079
ACETONE (2- PROPANONE)	67-64-1	452880	3.72	-0.23999999	1	30789
ALUMINIUM	7429-90-5	59400		0.33000001	3.2	1.1649E-7
ALUMINIUM PHOSPHIDE	20859-73-8	192000		-0.17	3.2	4.5199999E-9
ANTHRACENE	120-12-7	.5000002E-2	3.96	4.3400002	9120	0.001
ANTIMONY	1440-36-0				1475	0
ARSENIC	7440-38-2	380000			333	0
ASBESTOS	1332-21-4				1	0
BARIUM	7440-39-3	54800		0.23	260	
BENZENE	71-43-2	1780	550	2.1300001	6.7448001	12700
BENZO(a)ANTHRACENE	56-55-3	0.011	5.8109999E-2	5.9099998	40641.5	0.000028
BENZO(a)PYRENE	50-32-8	.8000001E-3	4.6500001E-2	6.04	54823.898	6.9999999E-7
BENZO(b)FLUORANTHENE	205-99-2	0.0151	1.2359999	6.0599999	141253.8	6.6699999E-6
BENZO(ghi)PERYLENE	191-24-2	0.00026	0.0146	6.6300001	25000	1.333E-8

Figure 2.6 Interface of contaminants data table

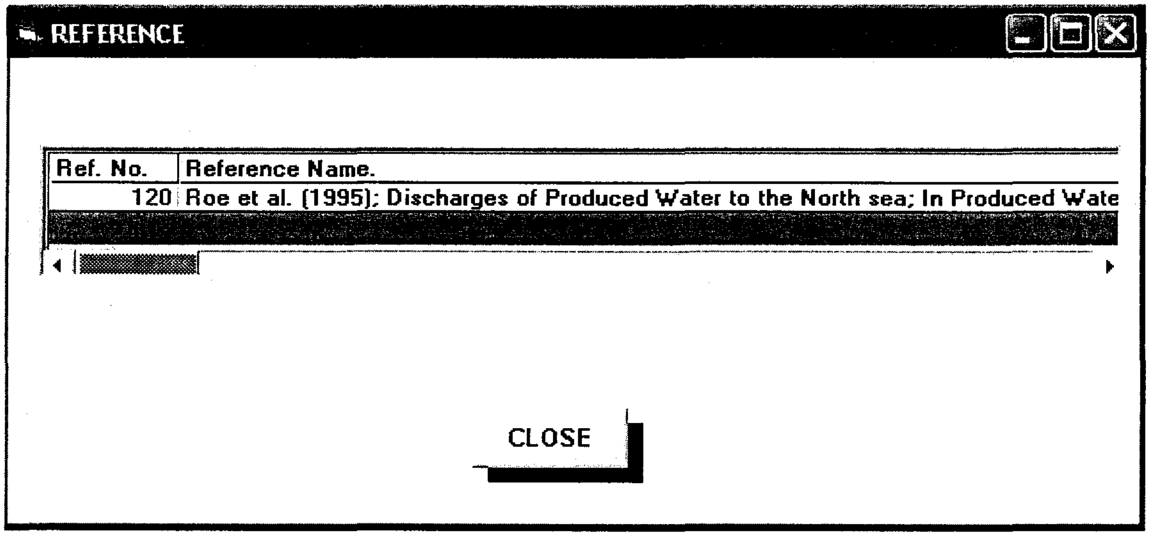


Figure 2.7 Interface of individual reference

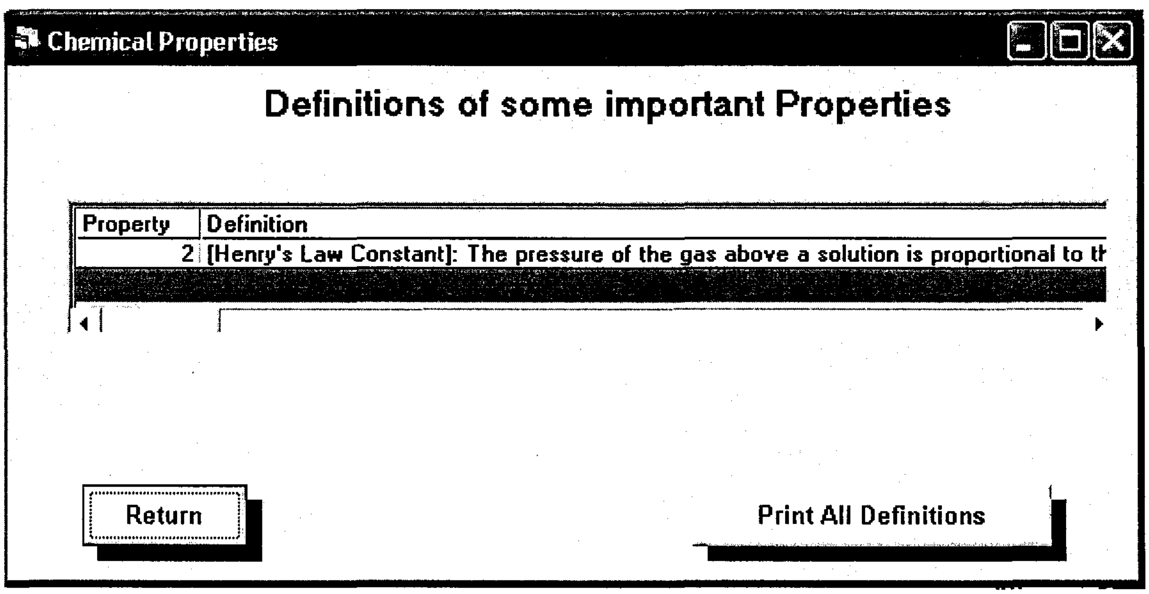


Figure 2.8 Interface of individual property definition

The full references can be accessed through a single command button. This is presented in Figure 2.9. All references and definitions can be printed by user-friendly commands. Any reference can be added or deleted. Figure 2.10 shows the form to add or delete any reference.

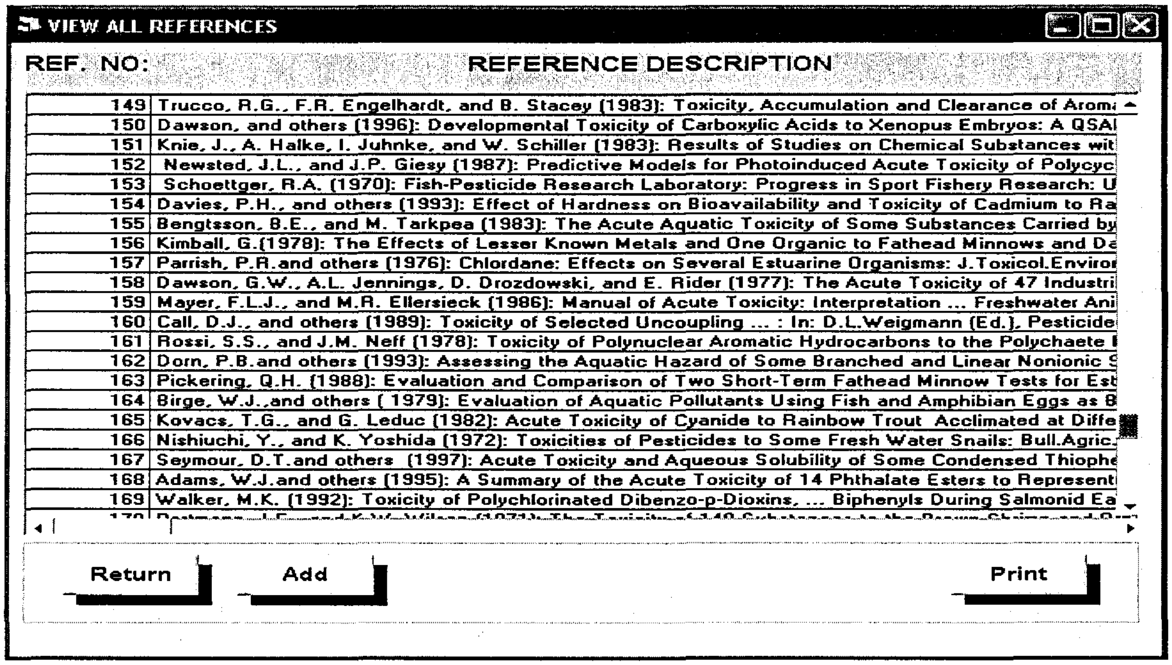


Figure 2.9 Interface of all references

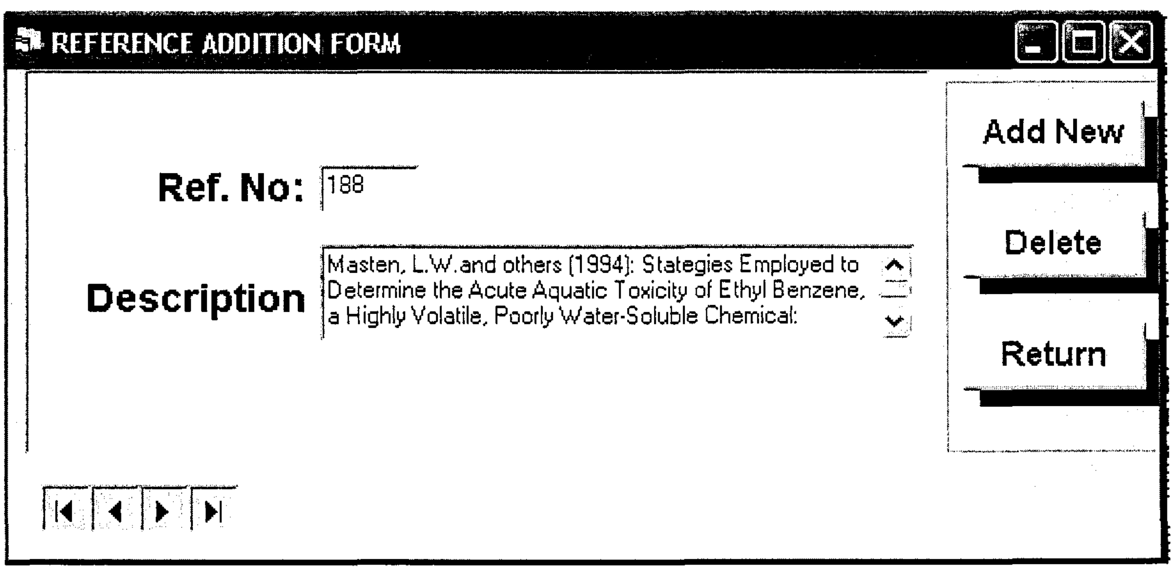


Figure 2.10 Interface of add/delete command execution

A contaminant can be selected through browsing the navigation commands or by direct query. If the name is typed partially or in full, related contaminants will be presented. The same purpose can be served by inserting the *CASRN* of the chemical in a specified format. The required contaminant can be accessed from that window. These are shown in Figures 2.11 and 2.12.

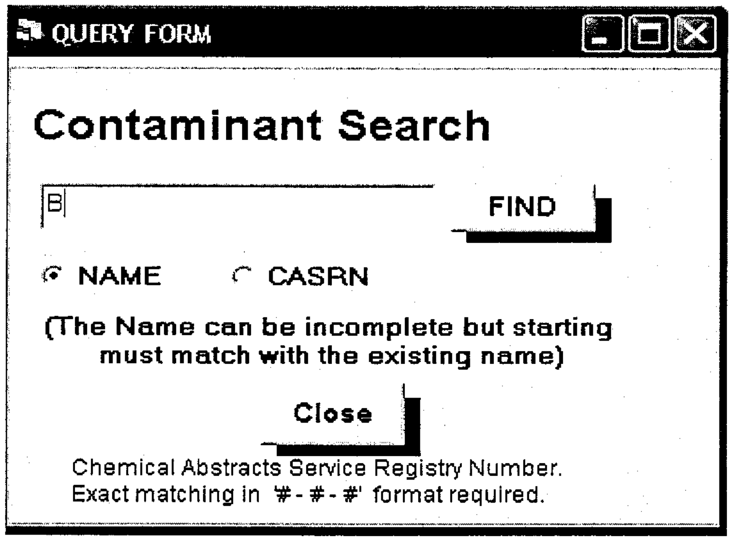


Figure 2.11 Interface of query form

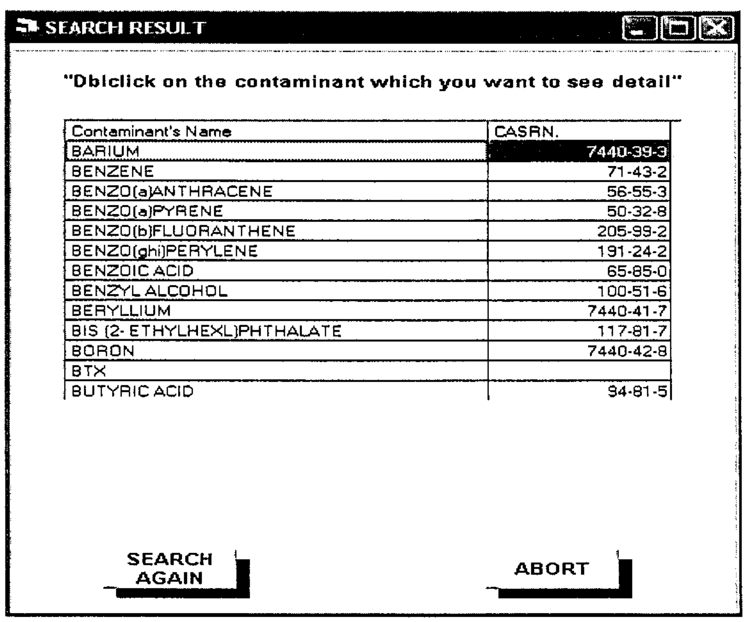
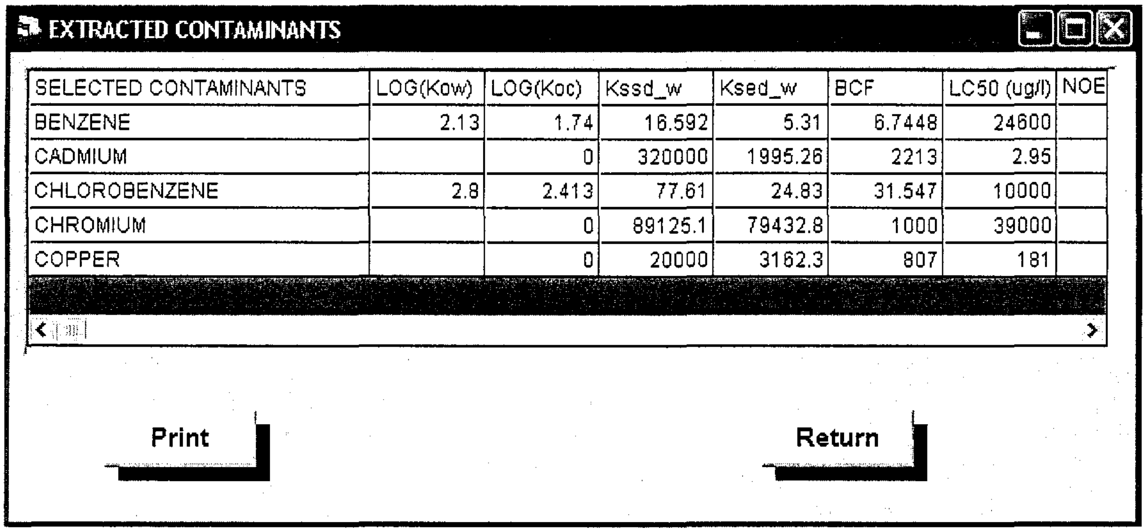


Figure 2.12 Interface of query result

Once the selection of contaminant(s) for analysis is done, the contaminant(s) can be viewed with selected properties in a window by clicking a command button. These can be printed if required. Figure 2.13 shows the necessary interface.



SELECTED CONTAMINANTS	LOG(Kow)	LOG(Koc)	Kssd_w	Ksed_w	BCF	LC50 (ug/l)	NOE
BENZENE	2.13	1.74	16.592	5.31	6.7448	24600	
CADMIUM		0	320000	1995.26	2213	2.95	
CHLOROBENZENE	2.8	2.413	77.61	24.83	31.547	10000	
CHROMIUM		0	89125.1	79432.8	1000	39000	
COPPER		0	20000	3162.3	807	181	

Figure 2.13 Selected contaminants' properties

A comprehensive database for the properties of produced water contaminants is presented in Appendix1.

2.5.2 Marine biota database

Selection of endpoints refers to the actual environmental value that is to be protected. Selection of endpoints is critical to problem formulation, which is the main part of ecological risk assessment (*ERA*). The endpoints are the focus of management and conceptual model development (USEPA, 1998). The selection of endpoints is guided by three criteria,

- Ecological relevance: The endpoints can be identified
- Susceptibility to known or potential stressors

- Relevance to management goals

The ecological risk assessment (*ERA*) will be discussed in Chapter 5. The most commonly selected endpoint for *ERA* is fish. In addition to fish, the regulatory agencies and other researchers (ANWQG, 2000; Reed et al., 1996; Sadiq, 2001; USEPA ECOTOX Database; Booman and Foyn, 1996; Reish et al., 1976-82) usually select different marine species including algae, shrimp, molluscs, bivalves. In the present work, a total of 25 different species have been selected in addition to fish, to compare lethality for the exposed condition. It is shown in Figure 2.14. Species *NOEC* and LC_{50} databases are presented in Appendices 2 and 3 respectively. The data for fish is presented in Appendix 1. The most dominant pathway for human uptake of contaminants is seafood ingestion.

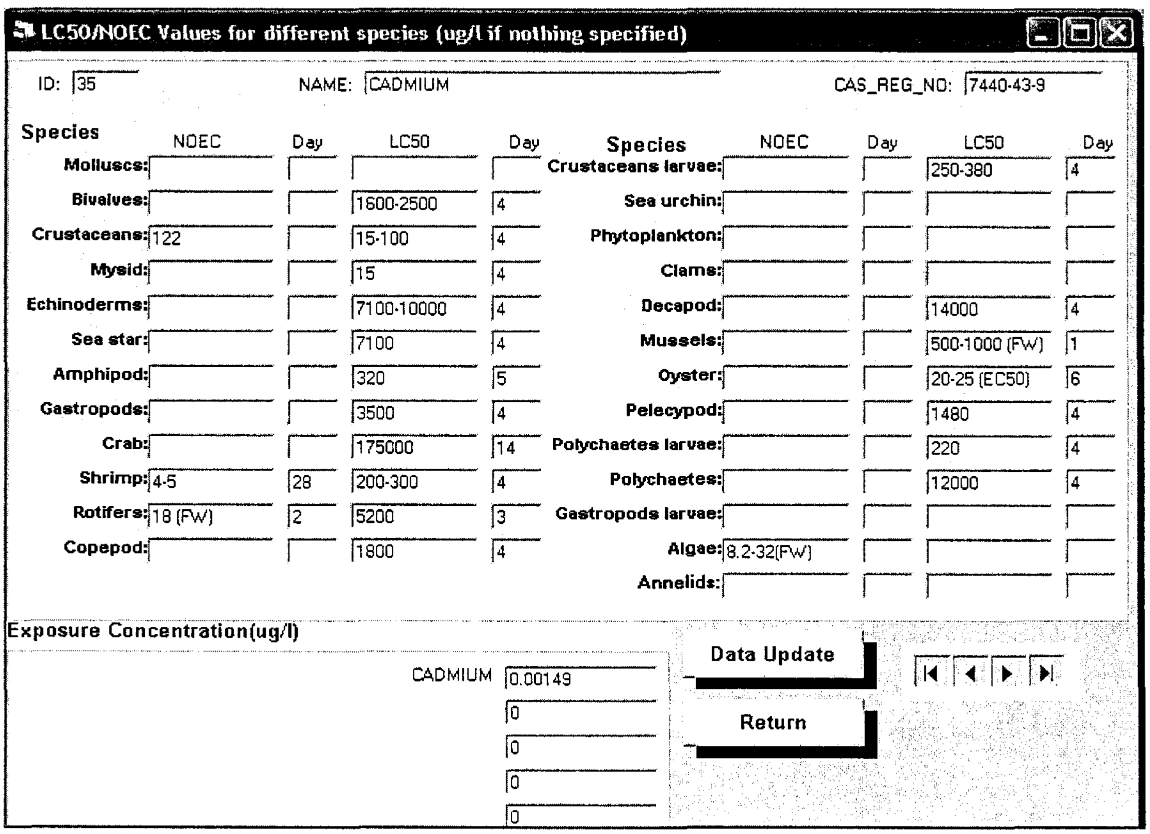


Figure 2.14 Endpoints species and their *NOEC* and LC_{50} with exposure period

2.6 Summary

The characterization of produced water has been emphasized in this chapter. The database developed for contaminants in produced water has been stored in the database section of the software. The database related interfaces are presented in this chapter. The limiting criteria for produced water discharges in different zones and the variability in physical and chemical properties have been discussed. Fish has been considered as the economically important marine species by numerous studies (ANWQG, 2000; Reed et al., 1996; Trefry et al., 1996). The average daily intake (*ADI*) of contaminants has been used to predict human health risk. Calculation of fish tissue concentrations is required to predict *ADI* in humans. These concentrations are used for the next steps of risk calculation. The growth of fish has been analyzed by using the models described in the following chapter.

Chapter 3

Development of Fish Growth Model

3.1 Introduction

Contaminants from produced water can be transported to the human body through ingestion of marine organisms including fish. Some contaminants may accumulate in human tissues or organs and can pose risk to human health. Exposure of migratory fish to produced water is a function of several factors like the sensitivity of fish to contaminants, and scope of fish migration from polluted zone to unpolluted zone. Unlike mammals, growth of fish is a continuous process throughout their life (Jones, 2002) and there occurs a change in lipid and bone contents depending on food availability and seasonal variation. By changing lipid and bone contents in the exposure period, growth plays an important role in accumulating contaminants in edible tissues. An approach to develop a model for fish growth has been considered in this study.

3.2 Model development framework

An empirical growth model has been developed in this study from data provided by Johnson (2000) and Falk et al. (1982). These data were collected from four different places during July, August and October 1999 along eastern Washington and from the NorthWest Territories in Canada for the Department of Fisheries and Oceans in 1979. The approach for model development is divided into four segments.

- Development of curvature and initial condition parameter models
- Age prediction from data using the Von Bertalanffy growth equation
- Development of length-weight model.
- Development of age-weight model

The segments are interrelated according to Figure 3.1.

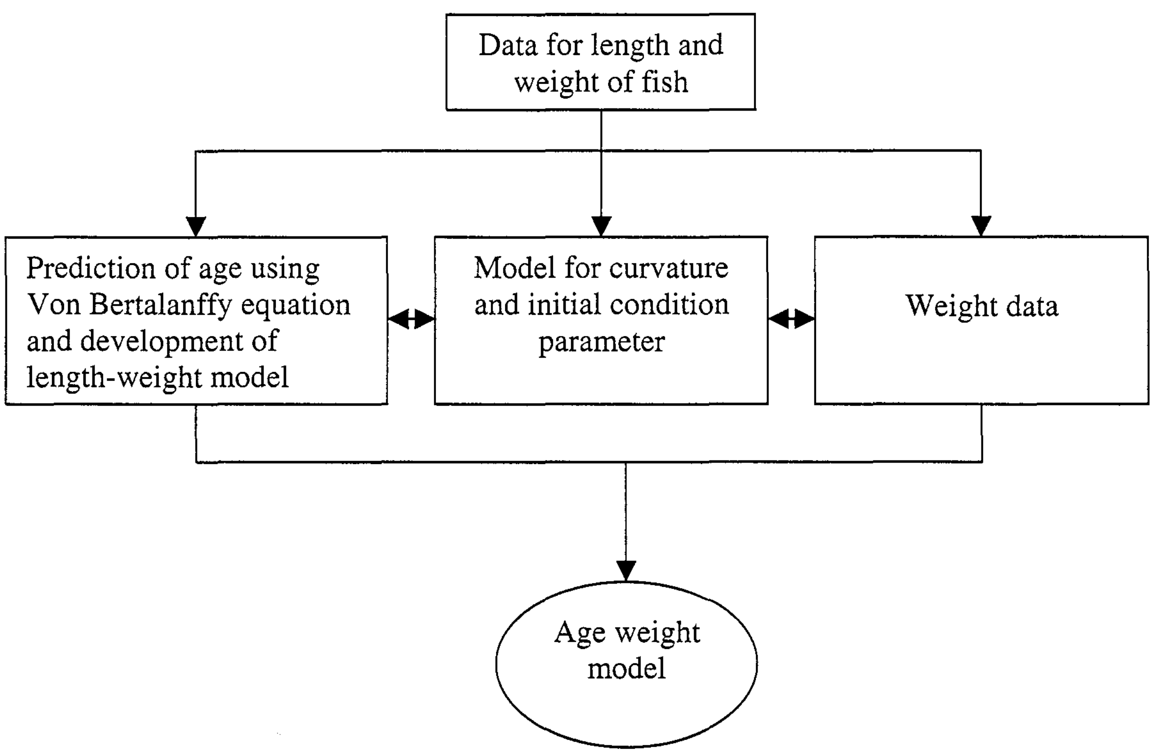


Figure 3.1 Model development framework

3.3 Fish age-length model

Numerous models of fish growth are available in the literature. A growth model developed by Pütter (1920) is considered the basis for other growth models (Sparre et al. 1998). Von Bertalanffy (1934) developed a growth model that has been shown to conform to the observed growth of most fish species and is widely used in research areas (Francis, 1996; Miller et al. 2000) because of its flexibility and consistency (Sparre et al. 1998). This function is the most commonly used growth function for adults (Jones, 2002). It has become one of the cornerstones in fishery biology because it is used as a sub-model in more complex models describing the dynamics of fish populations (Sparre et al. 1998). The Von Bertalanffy growth model is presented as

$$L_t = L_\infty (1 - e^{-k(t-t_o)}) \qquad (3.1)$$

where,

L_t = Fish length at age t (year)

L_∞ = Asymptotic length at infinitely long period

k = Curvature parameter (1/year)

t = Age in years

t_o = Initial condition parameter

The asymptotic length (L_∞) of fish is a hypothetical length at an infinite age. In reality, L_∞ for a species is considered as the available maximum length from the fish databases and literature (Miller et al. 2000). L_∞ depends on species type, food availability and other physical activities of the fish itself. The maximum size of Sea Trout is reported as 1400mm in Canada (FishBase, 2000). In the Baltic Sea, the maximum length for Trout (*Salmo trutta trutta*) is reported as 1420mm (Chrzan, 1959). In a study for Lake Superior, Miller et al. (2000) used L_∞ as 900mm for Trout. Available data from literature and databases on species maximum length is presented in Table 3.1.

Table 3.1 Maximum lengths of fish

Species name	Maximum Length (L_∞) mm	Source
Atlantic Cod	1410	USDOC (2003)
Haddock	880	USDOC (2003)
Ocean Pout	980	USDOC (2003)
Striped Bass	1020	USDOC (2003)
Trout	1420	Chrzan (1959)
Trout	1400	FishBase (2000)
Atlantic Mackerel	450	USDOC (2003)
Summer Flounder	780	USDOC (2003)
American Plaice	650	USDOC (2003)
Atlantic Halibut	1540	USDOC (2003)

The curvature parameter (k) that determines how fast the fish approaches its maximum length (L_∞), varies significantly with the asymptotic length consideration. Based on the maximum length and species, the values of k have been predicted in the range of 0.03 to 0.8 / year (FishBase, 2000). For relatively small fish, k is large and hence, within a year or two, most of the short-lived species reach their maximum length as shown in Figure 3.2. The other species have a flat growth curve with lower k and need many years to gain L_∞ (Sparre et al. 1998). The initial condition parameter (t_o) is the hypothetical age when a fish has zero length. This term does not have any biological significance as the growth starts at hatching when the larva already has a certain length, which may be called initial length at $t = 0$ on the day of birth. The parameter t_o has been found in literature to be between –2.14 to 0.152 year. For relatively smaller L_∞, t_o tends to be positive and for large L_∞ this value is negative (Figure 3.3). The parameters k and t_o vary with the asymptotic length of a fish species and thus can be defined as a set of parameters (Sparre et al. 1998). Typical variation of k and t_o with L_∞ is presented in Figure 3.3.

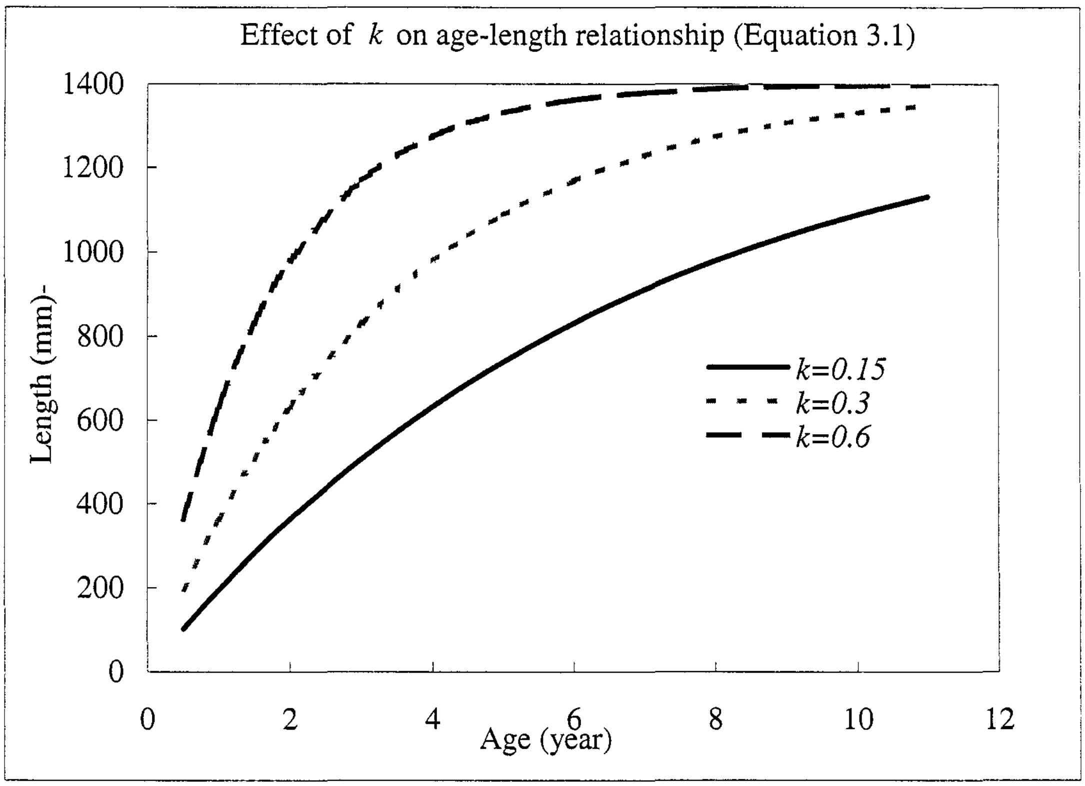


Figure 3.2 Effect of k on age-length relationship

The parameters for Trout (*salmo trutta trutta*) are tabulated in Table 3.2. Two equations were developed with R^2 values 0.89 and 0.91 respectively to predict the curvature parameter (k) and the initial condition parameter (t_o) from asymptotic length (L_∞).

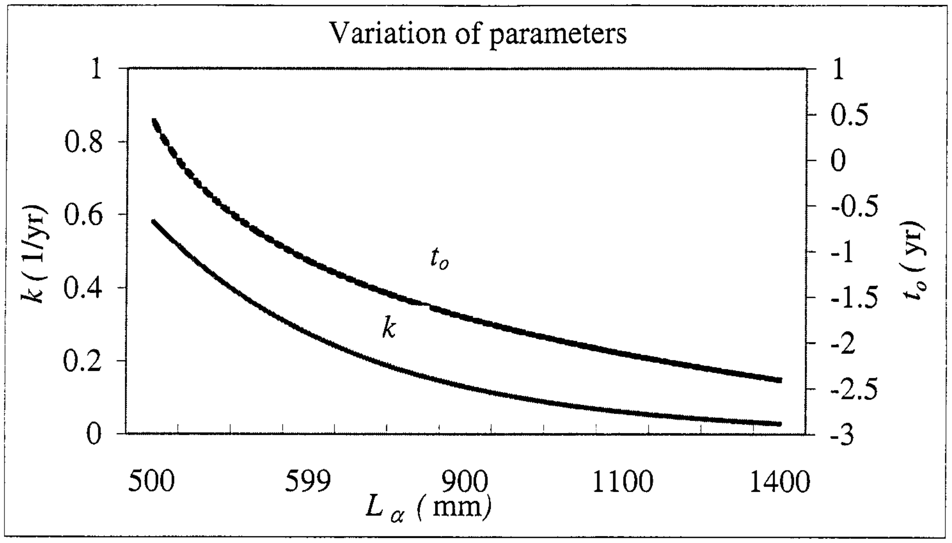


Figure 3.3 Variation of parameters L_∞, k, and t_o

The equations are presented as

$$k = e_1 \times exp\left(\frac{e_2}{L\infty}\right) \qquad (3.2)$$

$$t_o = e_3 + \frac{e_4}{L\infty} \qquad (3.3)$$

where,

k = Curvature parameter

L_∞ = Asymptotic length of fish (mm); in reality, it is the maximum length of fish.

e_1, e_2, e_3, e_4 = coefficients, predicted as 0.035 ± 0.023, 1490 ± 382, -2.47 ± 0.29 and 1164 ± 190 respectively by analyzing the data from Table 3.2 with the statistical software (Data fit).

The parameters k and t_o decrease exponentially with the increase of the asymptotic length of fish (shown in Table 3.2 and Figure 3.3). For L_∞ = 1400mm, k and t_o have been predicted using equations 3.2 and 3.3 as 0.10 and –1.64 respectively. A typical growth curve for Trout is shown in Figure 3.4.

Table 3.2 Parameters for fish length (source: FishBase, 2000)

Species	Asymptotic length (L_∞) mm	Curvature parameter k (1/year)	Initial condition parameter t_o (year)
Sea Trout	500	0.78	0.087
Sea Trout	570	0.4	-0.5
Sea Trout	599	0.4	-0.5
Sea Trout	599	0.34	-0.65
Sea Trout	700	0.21	-1.1
Sea Trout	1010	0.334	-1.06
Sea Trout	1190	0.108	-2.14
Sea Trout	1420	0.173	-1.69
Rainbow Trout	518	0.397	0.321
Rainbow Trout	744	0.383	0.624
Atlantic Cod	1320	0.09	-0.32
Atlantic Cod	1100	0.11	-0.48
Halibut	1870	0.07	-1.11

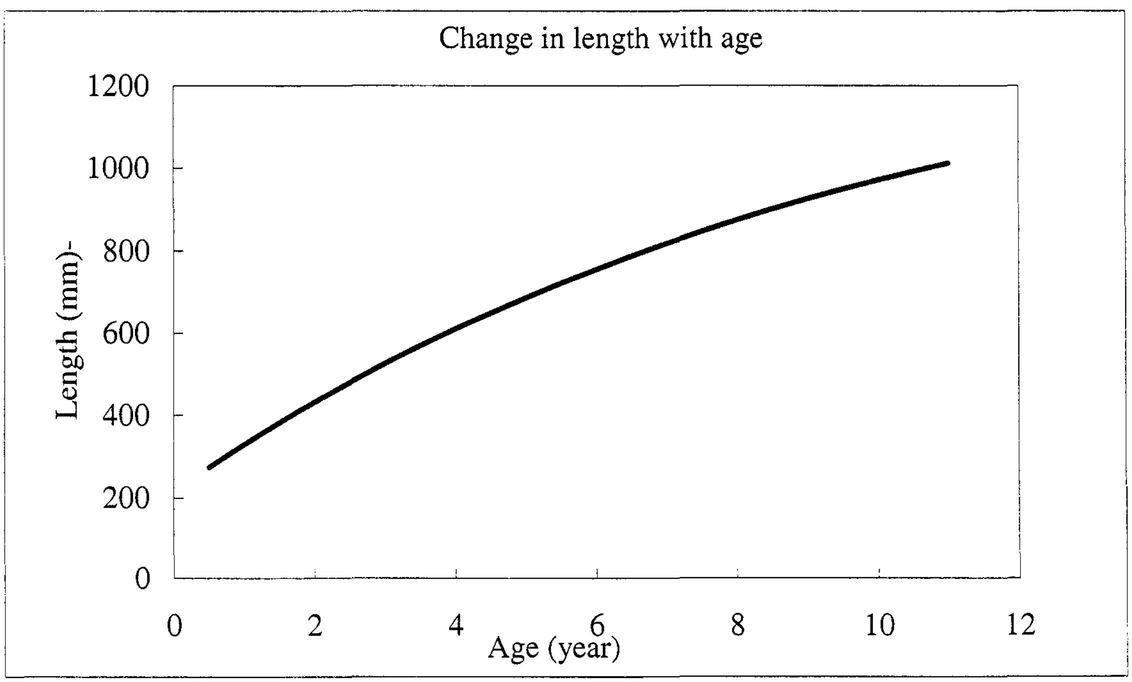


Figure 3.4 Length of fish with age

3.4 Fish length-weight model

When the body proportion, which is the ratio of body depth to length or head length to body length, remains constant, growth is referred to as isometric and where this ratio varies, the growth is called allometric (Jones, 2002). Numerous approaches have been made to develop a relationship between length and weight of fish. For isometric growth, a fish's biomass is a cubic function of its length and for allometric growth it does not follow the exact cubic functional relation (Jones, 2002). The generalized model equation can be written as

$$W_t = f_1 L_t^{f_2} \qquad (3.4)$$

where,

W_t = Weight at age t

f_1 = Growth parameter for particular species

f_2 =3 for isometric growth, otherwise allometric growth

L_t = Length at age t (year)

Most of the length-weight models have the general form of equation 3.4. The parameters f_1, f_2 vary with location, species, and other growth affecting factors such as food availability, migration from one zone to another zone and the ambient conditions. These parameters for length-weight model were compiled from different sources and are shown in Table 3.3. USDOC (2003) has a wide range of model collection for length-weight relationship that follows a similar form of equation (Equation 3.4). A similar effort to establish a relationship for the length and weight data from Johnson (2000) and Falk et al.

(1982) has been considered in this study. The parameters f_1 and f_2 vary in the range of 5.1×10^{-6} to 0.04 and 2.60 to 3.31 respectively based on the different species as shown in Table 3.3. American Plaice has the highest rates of weight changes in the length range of 30 to 650 mm (Table 3.3). The value of f_2 varies between 2.6 to 3.1 for Rainbow Trout and 2.92 to 3.1 for Atlantic Cod (Table 3.3).

The asymptotic length of Sea Trout on the basis of available data was considered and the corresponding k and t_o have been predicted using equations 3.2 and 3.3. The age of fish in the marine environment has been predicted using equation 3.1. Available statistical software was used to perform a non-linear regression to relate length and weight of a fish. Several polynomial and exponential models were verified in the analyses. The best-fit model to represent a length-weight relationship has a similar format as equation 3.4. The predicted coefficients are shown in Table 3.4. The values of the predicted parameters agree well with those in Table 3.3.

Table 3.3 Parameters for length-weight model

Species	Length range (mm)	f_1	f_2	Source
Halibut	1810	0.0195	3.0	Crawford et al.(1993)
Rainbow Trout	165-348	0.0063-0.0118	2.604-3.006	FishBase (2000)
Halibut	80-970	0.000005084	3.1904	USDOC (2003)
Rainbow Trout	325-691	0.0088	3.063	FishBase (2000)
American Plaice	30-650	0.000002904	3.3062	USDOC (2003)
Sea Trout	343-864	0.0038-0.0158	2.914-3.227	FishBase (2000)
Atlantic Cod	150-380	0.0041-0.0117	2.916-3.03	FishBase (2000)
Atlantic Cod	150-1060	0.0058	3.144	Thurow et al. (1982)
Brook Trout	58-323	0.0112	2.99	Carlander et al.(1969)
Cutthroat Trout		0.0434	2.825	Carlander et al.(1969)
American Plaice	100-360	0.0044	3.204	Coull et al. (1989)

Table 3.4 Predicted parameters for selected species

Parameter	Mean	90th percentile lower value	90th percentile upper value	Statistical software
f_1	4.04 E-05	2.3E-05	5.79 E-05	S Plus
f_2	2.82	2.76	2.88	S Plus
f_1	4.03E-05	2.33E-05	5.73E-05	Datafit
f_2	2.82	2.76	2.88	Datafit

The model has been fitted with an R^2 value of 0.97 and is presented in Figure 3.5. The model's goodness of fit was tested with available statistical functions. The residuals of the model development have been plotted on normal probability paper as shown in Figures 3.6 and 3.7.

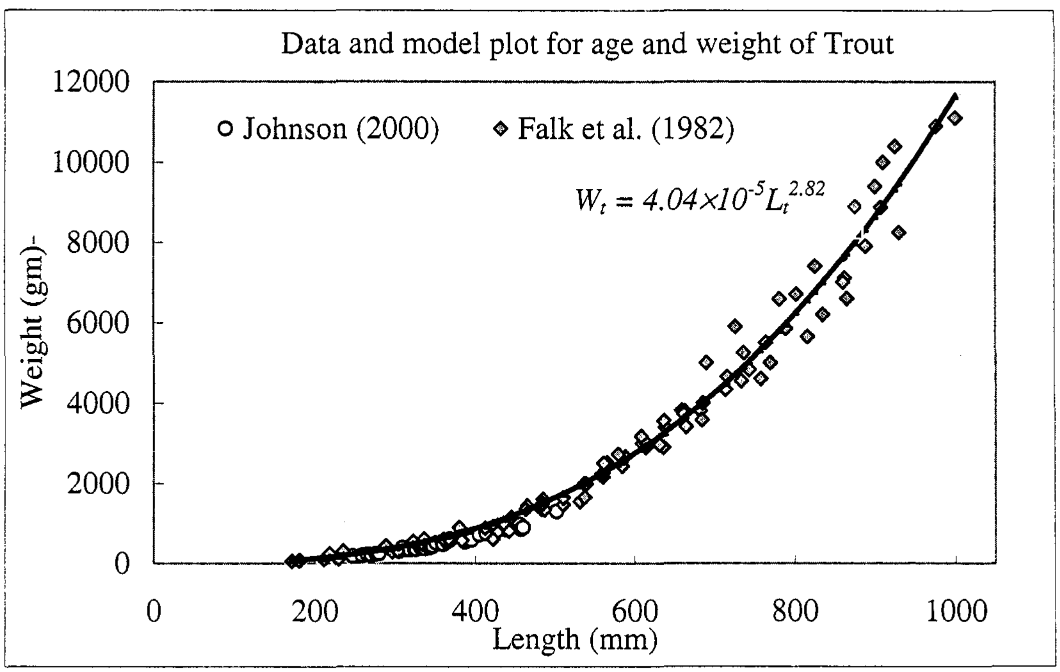


Figure 3.5 Length-weight model

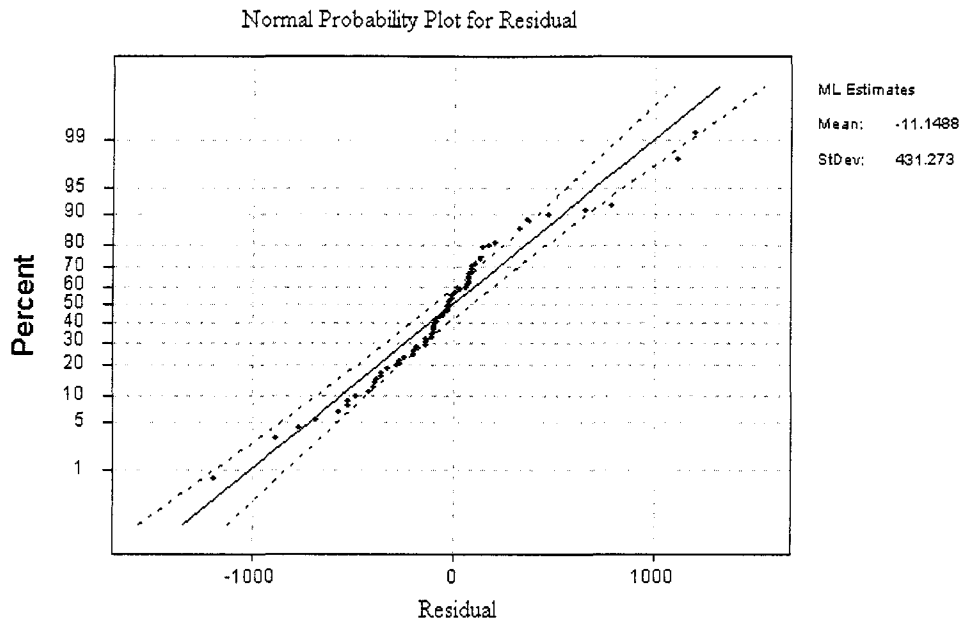


Figure 3.6 Probability plot of residuals in length-weight model

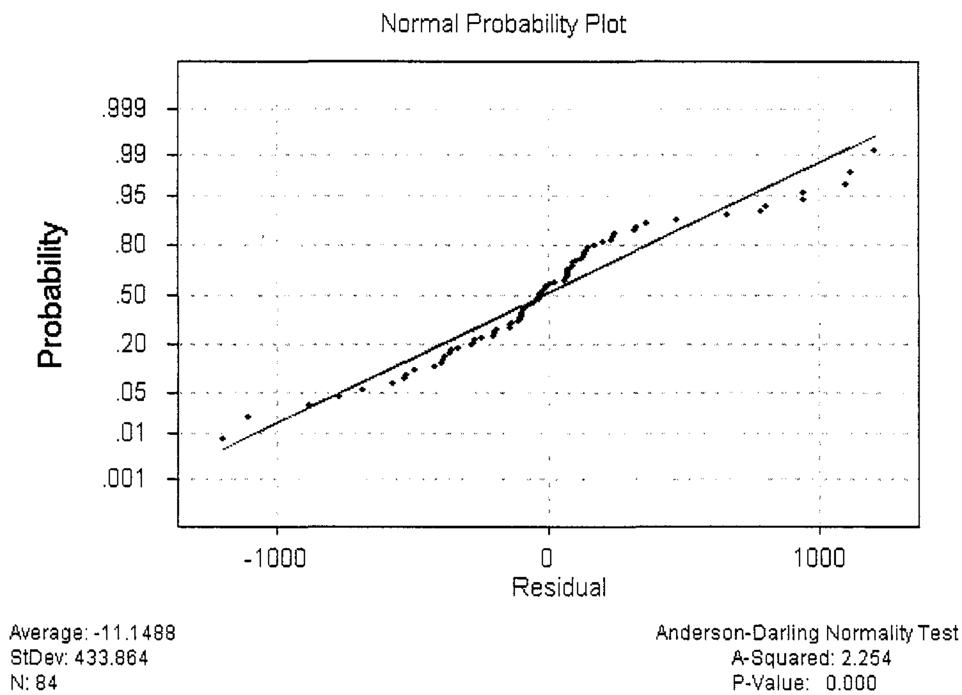


Figure 3.7 Normality test of residuals in length -weight model

3.5 Fish age-weight model

Growth is typically measured as the change in length or weight with the age of the fish. Growth of a fish is strongly influenced by the temperature of its environment, as well as food supply (Jones, 2002). Growth rate also depends on the type of measurement: whether length or weight of fish is measured. At a younger age, growth in length is less than that of the growth in weight (Jones, 2002). The simplest way to measure the growth rate over a period of time is to take the ratio of change in weight to the original weight. Mathematically,

$$g_1 = \frac{W_t - W_o}{t - t_o} \qquad (3.5)$$

where,

W_o = Weight at age t_o

W_t = Weight at age t

g_1 = Growth rate

This linear model gives a reasonable fit in the larval period but fails to model over longer periods (Laird et al. 1965). In periods when growth is accelerating; for example at intermediate sizes, the exponential growth rate fits better for instantaneous growth values (Jones, 2002). The growth rate in the intermediate stage of fish can be defined as

$$g_1 = \frac{\ln W_t - \ln W_o}{t - t_o} \qquad (3.6)$$

where,

t-t_o = Duration for which growth is to be predicted.

Equation 3.6 can be written as

$$W_t = W_o e^{g_1 (t - t_o)} \qquad (3.7)$$

The statistical data for different species fish indicates that the growth is not exponential throughout the entire lifetime of a fish (FishBase, 2000; USDOC, 2003; Jones, 2002). To predict growth, a better model is required (Jones, 2002). A general pattern of absolute growth for fish is slow when fish are small, fast when fish are at an intermediate size, and slow again as fish become large and begin to reproduce. This leads to an *S*-shaped or sigmoidal growth curve (Jones, 2002).

To express the *S*-shaped curve for weight at time *t*, a mathematical *S*-shaped function for the weight of fish (W_t) has been introduced as

$$Ln\left(\frac{W_t}{W_o}\right) = \frac{c}{a}\left(1 - e^{-at}\right) \qquad (3.8)$$

where,

a and c = Growth parameters that can be predicted through statistical analysis.

t= Age in years

W_o =Initial weight

W_t = Weight at age t

Equation 3.8 is a nonlinear equation and nonlinear regression must be performed to predict a and c. The least squares method of determining the parameters by minimizing the sum square error (SS_{res}) was employed to determine mean values of $\hat{a}$ and $\hat{c}$. The sum square error can be calculated as

$$SS_{res} = \sum_{i=1}^{n}\left(Ln\left(\frac{W_t}{W_o}\right) - \frac{\hat{c}}{\hat{a}}\left(1 - e^{-\hat{a}t}\right)\right)^2 \qquad (3.9)$$

To minimize the sum square error (SS_{res}), equation 3.9 was differentiated with respect to each parameter and set to zero, giving the following equations:

$$\sum_{i=1}^{n}\left(Ln\left(\frac{W_t}{W_o}\right)_i - \frac{\hat{c}}{\hat{a}}\left(1 - e^{-\hat{a}t}\right)_i\right)\left(\frac{\hat{c}\left(1 - e^{-\hat{a}t}\right)}{\hat{a}^2} - \frac{\hat{c}\,te^{-\hat{a}t}}{\hat{a}}\right)_i = 0 \qquad (3.10)$$

$$\sum_{i=1}^{n}\left(Ln\left(\frac{W_t}{W_o}\right)_i - \frac{\hat{c}}{\hat{a}}\left(1 - e^{-\hat{a}t}\right)_i\right)\left(-\frac{1 - e^{-\hat{a}t}}{\hat{a}}\right)_i = 0 \qquad (3.11)$$

Equations 3.10 and 3.11 are also nonlinear, so their solution requires an iteration process. The nonlinear function can be expanded into a Taylor series around an initial starting value and then the Gauss-Newton methods can be applied to estimate the parameters. The expanded Taylor series for equation (3.8) can be simplified as

$$Ln\left(\frac{W_t}{W_o}\right)_i - \frac{\hat{c}_0}{\hat{a}_0}\left(1 - e^{-\hat{a}_0 t}\right)_i \cong \gamma_1 \omega_{1i} + \gamma_2 \omega_{2i} \qquad (3.12)$$

where ω_{ji} is the derivative of the nonlinear function with respect to the jth parameter, γ_j is the difference between jth parameter's value and the starting value. The left side of equation 3.12 is the residual. In equation 3.12, γ_j is the regression coefficient and ω_{ji} is the regression variable. The linear regression structure built by Gauss-Newton procedure can be expressed as follows

$$y_i = \gamma_1 \omega_{1i} + \gamma_2 \omega_{2i} + \varepsilon_i \qquad (3.13)$$

where ε_I represents the model error term and

$$y_i = Ln\left(\frac{W_t}{W_o}\right)_i - \frac{\hat{c0}}{\hat{a0}}\left(1 - e^{-\hat{a0}\,t}\right)_i \qquad (3.14)$$

The parameters can be estimated using the following sequences:

a. Determination of the starting value of the *j*th parameter.
b. Estimation of γ_j from equation 3.13 using multiple least square.
c. Estimation of a new value of the *j*th parameter (add the increment with initial value).
d. Use the new *j*th value as the starting value.
e. Follow the process until convergence is reached.

This procedure can be carried out by several statistical packages. Statistical regression for nonlinear models for the dataset was performed by statistical software: S Plus and Datafit. The predicted values for the model fit are tabulated in Table 3.5.

Table 3.5 Parameters for age-weight model

Parameter	Mean	90^{th} Percentile Deviation	90^{th} percentile lower value	90^{th} percentile upper value	Statistical software
a	0.34	0.02	0.32	0.36	S Plus
c	1.59	0.05	1.54	1.64	S Plus
a	0.34	0.03	0.31	0.37	Datafit
c	1.6	0.04	1.56	1.64	Datafit

In both analyses, the mean values for the parameters are the same. There are negligible differences in the upper and lower limits of the parameters. The fitted model has an R^2 value of 0.99 and presented in Figure 3.8. Goodness of fit for the model was tested with a standard module in Minitab. The normal probability plot for residuals is presented in Figure 3.9 and the Anderson – Darling normality test for the residuals was performed in Minitab. The resulting P value was 0.00 and mean was approximately zero as presented in Figure 3.10.

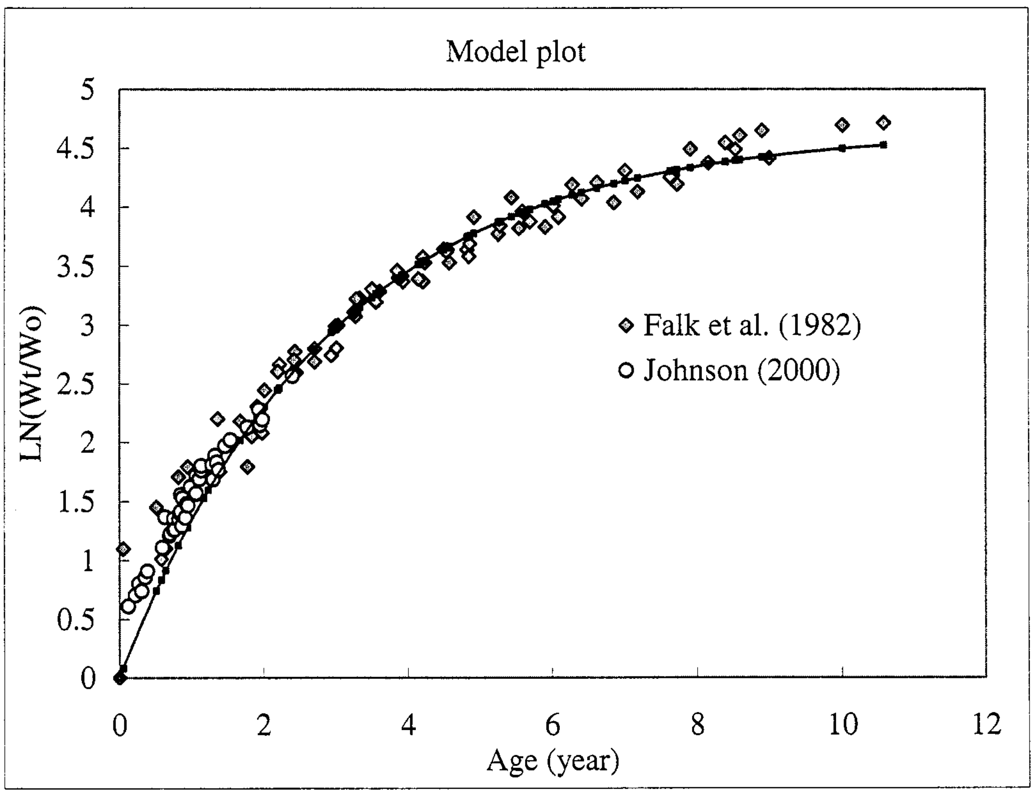


Figure 3.8 Age-weight model for fish growth

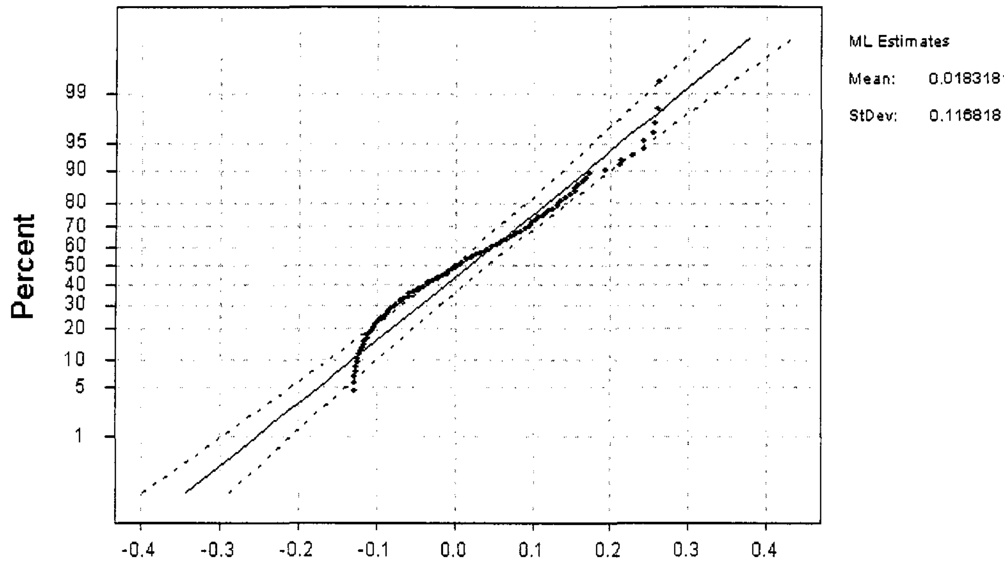


Figure 3.9 Normal probability plot residuals for fish growth model

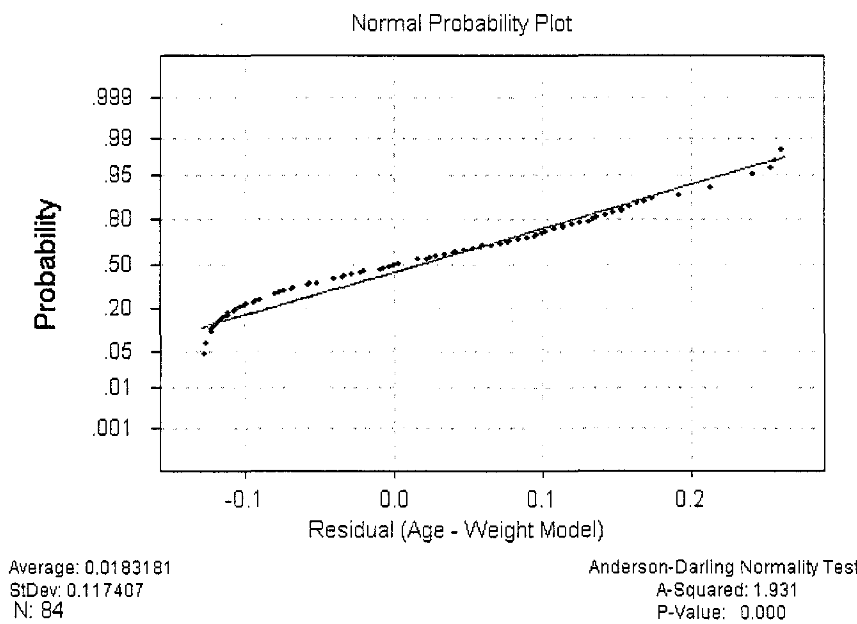


Figure 3.10 Plot for Anderson-Darling Normality test of residual

The ratio between mean a and c was constant in both analyses by Datafit and S Plus softwares. Replacing the coefficients in equation 3.8 by the estimated values and introducing the error term, the equation 3.8 can be rewritten as

$$Ln\left(\frac{W_t}{W_o}\right) = \frac{\hat{c}_0}{\hat{a}_0}\left(1 - e^{-\hat{a}_0 t}\right) + \varepsilon \qquad (3.15)$$

where, the error term ε is approximately normally distributed with a mean about zero and a standard deviation of 0.12. Setting the values of the parameters, the models can be presented as

$$Ln\left(\frac{W_t}{W_o}\right) = \frac{1.59}{0.34}\left(1 - e^{-0.34\,t}\right) \qquad (3.16)$$

$$Ln\left(\frac{W_t}{W_o}\right) = \frac{1.59 \pm 0.05}{0.34 \pm 0.02}\left(1 - e^{-(0.34 \pm 0.02)t}\right) + N(0, 0.12) \qquad (3.17)$$

Similarly, the data was analyzed with polynomial, inverse polynomials, concave/convex function, and exponential function using S Plus and Datafit software. However, those models did not fit well with the data and the goodness of fit tested by Minitab did not support those types of models. The model in equation 3.16 and 3.17 has been identified as the best-fit model.

Equation (3.16) is a single output equation that works deterministically for a given set of parameters on the basis of an average value. On the other hand, equation (3.17) deals with error term ε, and an uncertainty measure of the model through incorporating mean ± standard error for the parameters. In predicting body weight of a fish, uncertainty could arise from different sources including, but not restricted to data uncertainties, model uncertainties, species variability, feeding patterns of different fish species, surrounding environment, and migration activities. Since deterministic models cannot incorporate related uncertainties (Lee and Cheung, 1991; Wood, 1993), a probabilistic concept has been introduced. The parameters can be determined mathematically by converting the scale of equation 3.8 and then plotting on graph paper as follows.

$$\frac{a}{c} \times Ln\left(\frac{W_t}{W_o}\right) = \left(1 - e^{-at}\right)$$

$$\Rightarrow Ln\left(1 - \frac{a}{c} \times LN\left(\frac{W_t}{W_o}\right)\right) = -at$$

$$\Rightarrow Ln\left(1 - k_1 \times LN\left(\frac{W_t}{W_o}\right)\right) = -at$$

$$\Rightarrow \boldsymbol{Y = m\,X} \qquad (3.18)$$

where,

$$k_1 = \frac{a}{c}$$

$$Y = Ln\left(1 - k_1 Ln\left(\frac{W_t}{W_o}\right)\right)$$

$$m = -a$$

Modeled weight for Trout is plotted in Figure 3.11. The models can be used to predict weight of fish during an exposure period. However, the parameters a and c are not constant for all species and thus particular species statistical data need to be analyzed for predicting the values of the parameters. The parameters a and c are not independent and therefore can be treated as a set of parameters. Trout may achieve 2 to 5 kg weight within 3 to 6 years of age in normal environmental conditions when most of the fishes are caught for commercial purposes (Huet, 1986). The developed models (equations 3.16 and 3.17) may be used to predict the weight of up to 7-year-old fish with good statistical agreement. For older fish, further study is required to model the weight of fish.

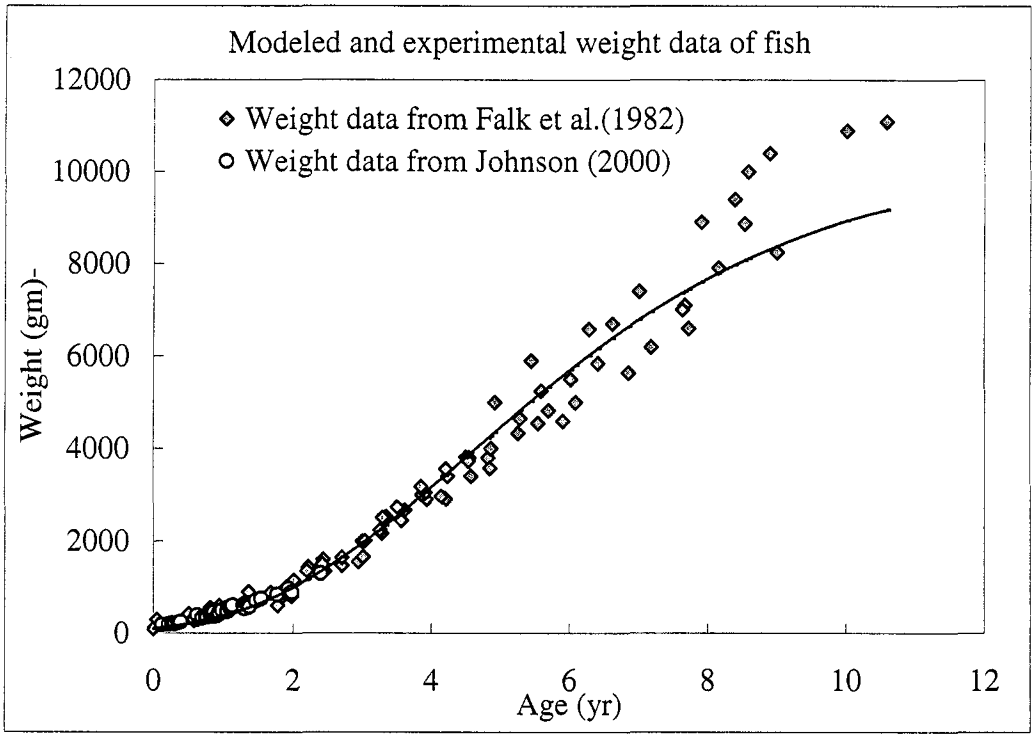


Figure 3.11 Modeled weight of Trout with age

The initialization of human health risk prediction from produced water starts with prediction of contaminants' concentration in the edible parts of fish. As the growth of fish is a continuous process, the weight of the edible parts varies within the exposure duration in the contaminated zone. The fraction of lipid in a fish is a seasonally variable factor (Campbell et al. 1988; Madenjian et al. 2000) that varies within 0.5 to 12% (USEPA 1996a) and thus use of snapshot lipid content does not represent the variability.

Prediction of contaminants' concentration in fish follows several interrelated methodologies. The USEPA, (2000) calculates the concentration in fish tissue as

$$C_{exp} = C_w \times p \times BAF \qquad (3.19)$$

where,

C_{exp} = Exposure concentration for fish

C_w = Concentration of contaminants in water

p = Exposure probability

BAF = Bioavailable fraction

Relating this exposure concentration with bioconcentration factor, concentration in fish is calculated as

$$C_f = C_{exp} \times BCF \times Fr \qquad (3.20)$$

where,

C_f= Fish tissue concentration

BCF = Bioconcentration factor

Fr =Fraction of lipid in fish

In this approach, the snapshot lipid content inherits uncertainty due to its variability across the species and seasons (Campbell et al. 1988; Madenjian et al. 2000). As discussed in Chapter 2, metals have higher bioconcentration factors and therefore can be accumulated in the fish tissue by several orders of magnitude more than those in the media (Campbell et al. 1988). Metal also shows multicompartmental distribution within invertebrate tissues and thus is transported from tissue to tissue (Campbell et al. 1988); hence metal can be transported from lipid to flesh. Most of the metals are stored in an inactive form within lipid and tissues (Campbell et al. 1988) and thus their accumulation in bones is not significant (Campbell et al. 1988; Eisler 2002). The assumption of metals distributions in the whole body of fish would predict lower concentration of contaminants in fish tissue. The equation 3.20 does not consider the edible part in a fish, which varies in the range of 64 to 87% of the whole body weight (USEPA, 1996a). This needs to be incorporated for more realistic prediction of fish tissue concentration.

As the growth of fish occurs, contaminants uptake varies in different stages of growth and thus the accumulation of contaminants in fish tissue varies. The fish growth models assist in predicting contaminants concentration in fish tissue and thus play an important role in human health risk assessment from fish consumption. A fish can uptake contaminants through its gills, skin and food chain and release these through excretions, the mouth and other physical activities (Campbell et al. 1988). Contaminant uptake is affected by several factors like temperature, salinity, gills capacity, passage through the intestines and others. Other than the uptake phenomena, the cumulative accumulation of contaminants is the focus of the study. To incorporate the variability for the fish tissue concentration calculation, the change in the edible part of fish within an exposure period needs to be incorporated. The distribution of total accumulated contaminants throughout the edible parts will provide more realistic prediction. The application of the models is discussed in the following chapters.

3.6 Summary

The empirical models of fish growth have been discussed in this chapter. To develop the growth models, a number of primary models, including the curvature parameter and initial condition parameter models have been developed. The age of fish was calculated using the Von Bertalanffy growth function (equation 3.1). The experimental data of fish weight was modeled with the calculated age and deterministic and probabilistic forms of the models have been developed as in equations 3.16 and 3.17. The importance of the growth models in relation to lipid and edible parts of fish is discussed in this chapter.

Chapter 4.

Model Selection and Integration of Models with the Software

4.1 Introduction

Once produced water is discharged into the ocean, it mixes with the ambient water and becomes diluted. The aromatic hydrocarbons in treated produced water are attenuated rapidly in the marine environment (OGP, 2002) due to advection, dispersion and diffusion as a result of ocean environmental conditions. Field studies and dispersion modeling of the fate of produced water in the North Sea show a typical initial dilution of 1000 fold within 50 to100 meters of the discharge point (Furulolt, 1996; Riksheim and Johnsen, 1994). The volatile *BTEX* compounds, the most abundant aromatic compounds in produced water, evaporate rapidly upon mixing with the surface water (OGP, 2002). In the Norwegian sector of the North Sea, a 1996 study on effects of polycyclic aromatic hydrocarbons (*PAHs*) on a caged fish placed 500m downstream from a major discharge location resulted in no significant biological effects to that fish (OGP, 2002). The biodegradation half lives of aromatic compounds range from less than a day to several months (Johnsen et al. 2000) and thus significant amounts and varieties of aromatic hydrocarbons fall below the risk level within a very short period of time after the discharge. Certain amounts and varieties of contaminants, including the heavy metals, non-volatile and semi-volatile chemicals, and the process chemicals that are still present in the produced waters may pose risk to ecological entities and health hazards to humans through the food web.

In the Gulf of Mexico, zero discharge of produced water within 3 miles of the structures was imposed in both *BAT* and *NSPS* regulatory options (USEPA, 1993), which is an acknowledgement of environmental impacts from offshore operations. The arrangements of discharging produced water at a distance of more than 3 miles from the structures are costly and feasibility depends on the ambient ocean characteristics. Some offshore oil producing platforms inject produced water into the underlying soil strata. This technique is site-specific and the performance depends on the porosity of the underlying soil strata and their absorption capacity as well as their permeability. These are limited to areas such as Cook Inlet, Alaska and some platforms in Norway.

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 a result of the difference in the momentum flux, the effluent discharge can be characterized as a buoyant jet flow (Mukhtasor, 2001). The risk associated with the contaminants discharged with the produced water depends strongly on the contaminants' fate and distribution in the ambient seawater (Somerville et al., 1987; Meinhold et al., 1996; Karman and Reerink, 1998), which mainly depend on hydrodynamic characteristics, discharge geometry and the ambient seawater flow characteristics. Field measurements are the best methods to assess a contaminant's concentration in the surrounding areas for risk assessment purposes, although the feasibility, cost and time required for the fieldwork can be prohibitive. Moreover, the field measurements can be employed after the platforms start discharging produced water and in most cases, it is impossible or impractical to measure field concentration continuously throughout the whole area of the contaminants' dispersion.

To assess contaminants' concentrations for risk assessment purposes, hydrodynamic modeling plays an important role (Lee et al. 1991; Huang et al. 1994, 1996; Mukhtasor, 2001) and therefore development of hydrodynamic modeling for initial dilution and dispersion has achieved much attention in recent years. The plume trajectory and turbulent diffusion, in addition to initial dilution is also an important measure for hydrodynamic modeling (Somerville et al. 1987). The major weakness of currently available ecological risk assessment (*ERA*) models is their inability to define the whole scenario induced by a produced water contaminant based on selected endpoints that need to be protected.

In developing hydrodynamic models, the mixing of produced water has been conceptualized as two separate regions (Lee et al. 1991; Mukhtasor, 2001). The first region, where the discharge trajectory, momentum flux and geometry play important roles is known as the near field *(NF)*. The other region, in which the ambient characteristics become important, is known as the far field *(FF)*. In the far field, the trajectory and dilution are mainly controlled by ambient water characteristics, such as the strength and direction of seawater currents, and through buoyant spreading motions and passive diffusion (Doneker and Jirka, 1990).

4.2 Various dilution models

Numerous dilution models are available for initial dilution prediction. The available models, their feasibility and scope of applications are discussed in this section.

Dilution model by Lee and Cheung (1991): The jet behavior for a buoyancy dominated discharge is governed by the dimensionless depth zu^3/B where B is the discharge buoyancy, u is the ambient current velocity and z is the depth above discharge. The buoyancy length scale l_b is defined as B/u^3 and B is defined as $Q\ (\Delta\rho_j / \rho_a)\ g$, where Q is the source volume flux and is equal to $u_j \pi d^2/4$, where u_j is the exit velocity of jet, d is the diameter of the exit pipe, $\Delta\rho_j$ is the density difference between the ambient water (ρ_a) and effluent (ρ_e) and is defined as $(\rho_a - \rho_e)$ and g is the acceleration due to gravity. Two length scales are used in this model, in which, l_Q is the measure of direct effect of jet geometry on flow characteristics and l_M is the measure of the distance where buoyancy becomes more effective than the jet momentum.

$$l_Q = d\left(\frac{\pi}{4}\right)^{1/2} \qquad (4.1)$$

$$l_M = \frac{M^{3/4}}{B^{1/2}} \qquad (4.2)$$

For $z / l_Q >> 1$, the volume flux is not important, so the dilution changes to

$$S = f\,(z/l_b) \qquad (4.3)$$

where,

S = Centerline dilution (dimensionless)

For $(z/l_b<<1)$, the dilution equation for the buoyancy-dominated near field (*BDNF*) is given by

$$\frac{SQ}{ul_b^{\ 2}} = C_1\left(\frac{z}{l_b}\right)^{5/3} \qquad (4.4)$$

For $(z/l_b>>1)$, the dilution equation for the buoyancy-dominated far field (*BDFF*) is given by

$$\frac{SQ}{ul_b^{\ 2}} = C_2\left(\frac{z}{l_b}\right)^{2} \qquad (4.5)$$

where,

C_1, C_2 = Constants

The average values for C_1 and C_2 were determined to be 0.10 and 0.51 respectively. The dilution characteristics within the transition zone were merged into near field and far field models. No specific solution was incorporated to predict the dilution in the transition zone.

Dilution model by Lee and Neville-Jones (1987): Lee and Neville-Jones (1987) presented the following models for minimum surface dilution based on the field data for horizontal buoyant jets at a number of United Kingdom outfalls:

$$\frac{SQ}{ul_b^{\ 2}} = 0.31\left(\frac{z}{l_b}\right)^{5/3} \quad (\text{BDNF}, z/l_b < 5) \qquad (4.6)$$

$$\frac{SQ}{ul_b^{\ 2}} = 0.32\left(\frac{z}{l_b}\right)^{2} \quad (BDFF, z/l_b \geq 5) \qquad (4.7)$$

where,

S = Centerline dilution in the boil center

z = Water depth above the discharge

The flow characteristics in the transition zone were ignored in this model.

Dilution model by Proni et al. (1994): Proni et al. (1994) suggested the dilution model as

$$\frac{SQ}{ul_b^{\,2}} = 0.15\left(\frac{z}{l_b}\right)^{5/3} \quad (BDNF,\ z/l_b < 0.1) \qquad (4.8)$$

$$\frac{SQ}{ul_b^{\,2}} = 0.32\left(\frac{z}{l_b}\right)^{2} \quad (BDFF,\ z/l_b \geq 0.5) \qquad (4.9)$$

For the transitional regime between the *BDNF* and *BDFF*, the power law equation was developed as

$$\frac{SQ}{ul_b^{\,2}} = \xi\left(\frac{z}{l_b}\right)^{\eta} \qquad (4.10)$$

where,

ξ, η = Site-specific constants

η varies between 5/3 to 2 and ξ can be predicted as a regression coefficient. The only differences between this model and the Lee and Cheung (1991) model are in the coefficients and parameter (z/l_b) ranges for *BDNF* and *BDFF*.

Dilution model by Huang et al. (1998): Huang et al. (1998) developed a centerline initial dilution model that covers all the flow regimes, from the buoyancy dominated near field (*BDNF*) through the intermediate regime to the buoyancy dominated far field (*BDFF*) with a single equation. The model equation is as follows

$$\frac{SQ}{uz^2} = b_1\left(\frac{z}{l_b}\right)^{-1/3} + \frac{b_2}{1 + b_3\left(\frac{z}{l_b}\right)^{-d_2}} \qquad (4.11)$$

where,

b_1, b_2, b_3 and d_2 = Model constants.

z = Height above discharge.

The values of C_1 and C_2 from Lee and Cheung (1991) were substituted for b_1, b_2 respectively. The other two constants b_3 and d_2 were predicted as 0.1 and 2 respectively. The equation is able to provide dilution at any regime of buoyancy dominated near field (*BDNF*), transition and buoyancy dominated far field (*BDFF*). The prediction of constants b_3 and d_2 was based on trial and error, which is not a standard procedure for predicting coefficients. For the *BDNF* region, the dilution is the same as that of Lee and Cheung (1991) but for higher z/l_b (>0.5), the dilution is higher than that of Lee and Cheung (1991). The dilution models are plotted in Figure 4.1.

Dilution model by Mukhtasor (2001): Mukhtasor (2001) developed a model for outfall dilution based on the model relating initial dilution in terms of SQ/uz^2 and z/l_b only as proposed by Huang et al. (1998). The model equations were developed as

$$\frac{SQ}{uz^2} = 0.13\left(\frac{z}{l_b}\right)^{-0.31} + 0.46e^{\frac{-0.22}{z/l_b}} \qquad (4.12)$$

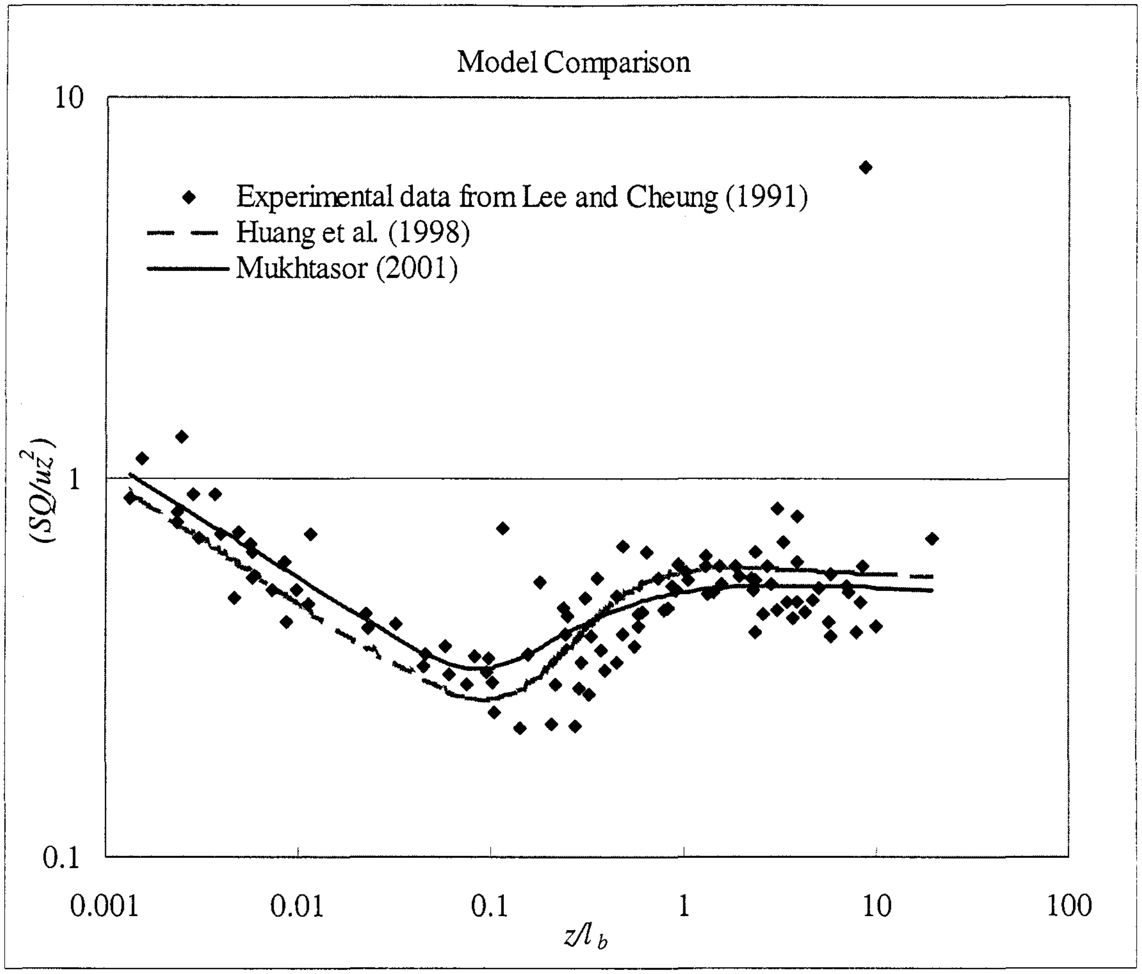


Figure 4.1 Plot of dilution model for Huang et al. (1998) and Mukhtasor (2001) and experimental data from Lee and Cheung (1991)

$$\frac{SQ}{uz^2} = (0.13 \pm 0.02)\left(\frac{z}{l_b}\right)^{-0.31 \pm 0.03} + (0.46 \pm 0.02)\exp\left(\frac{-0.22 \pm 0.04}{z/l_b}\right) + N(0, 0.092) \qquad (4.13)$$

$$l_b = \frac{Qg}{u^3}\left(\frac{\rho_a - \rho_e}{\rho_a}\right) \qquad (4.14)$$

where,

S = Initial centerline dilution

Q = Effluent discharge (m^3/sec)

u= Ambient water velocity (m/sec)

$N(0,0.092)$= Normally distributed error term with mean 0 and standard deviation 0.092

z= Height of water surface from discharge point (m)

l_b= Vertical distance at which the effluent velocity is reduced to ambient velocity (m)

g= Acceleration due to gravity =9.81 m/sec^2

ρ_a= Ambient water density (kg/m^3)

ρ_e= Effluent density (kg/m^3)

In this equation, both the buoyancy dominated near field (*BDNF*) and buoyancy-dominated far field (*BDFF*) are connected through the transition zone and thus these models are able to predict dilution at any regime including the buoyancy-dominated near field, transition zone and buoyancy-dominated far field. The near field mixing is applicable for deep-water conditions where a distinct buoyant jet rises to the surface and dilution occurs as a result of turbulent jet entrainment (Jirka and Lee, 1994). The deep-water condition is defined as

$$\frac{H}{d} > 0.22F_o \qquad (4.15)$$

William (1985) defined F_o as

$$F_o = \frac{V_j}{\sqrt{gd\frac{\rho_a - \rho_e}{\rho_a}}} \qquad (4.16)$$

where,

H = Depth of the ambient water (m)

d = Diameter of the port (m)

F_o = Froude Number.

Equation 4.15 has minimum sensitivity to the discharge angle (Jirka and Lee, 1994). The inability of the discharge to satisfy the above condition (Equation 4.15) may return instability and thus a local circulation zone can be developed which is generally avoided to achieve maximum initial dilution (Hamdy, 1981). The local instability is presented in Figure 4.2 (Tsanis and Valeo, 1994). The general characteristics of discharge from a horizontal outlet pipe close to bottom is to touch the floor tangentially and the particles near the boundary layer impinge on the sea bed. Discharge from a vertical outlet exits vertically at high speed and the plume is weakly deflected until the plume velocity approaches the ambient velocity. When the jet velocity approaches the ambient velocity, it bends in the direction of ambient current. The length at which the plume velocity becomes less important and the ambient current start advecting the plume is called the length scale l_b. These are shown in Figures 4.3 and 4.4 respectively.

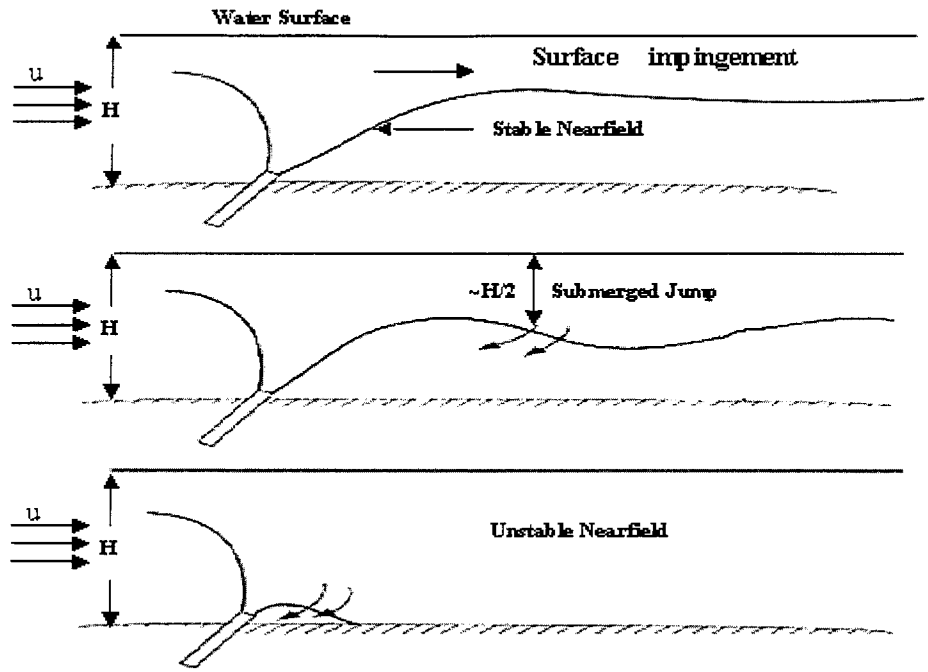


Figure 4.2 Local instability of effluent flow (Modified after Tsanis and Valeo, 1994)

For a stable discharge from an open-ended outfall into unstratified running water, the initial dilution predicted by Mukhtasor's model (equations 4.12 and 4.13) agrees reasonably well with the other models described above.

The horizontal distance at which the plume impinges on the surface and deflects to follow the ambient current direction is called the boil center as presented by Wright (1977 b) as

$$x_{b1} = \frac{C_3 z^{4/3}}{l_b^{1/3}} \qquad (4.17) \qquad \text{For } z << l_b \ (BDNF)$$

$$x_{b2} = \frac{C_4 z^{3/2}}{l_b^{1/2}} \qquad (4.18) \qquad \text{For } z >> l_b \ (BDFF)$$

where,

C_3 and C_4 = Constants

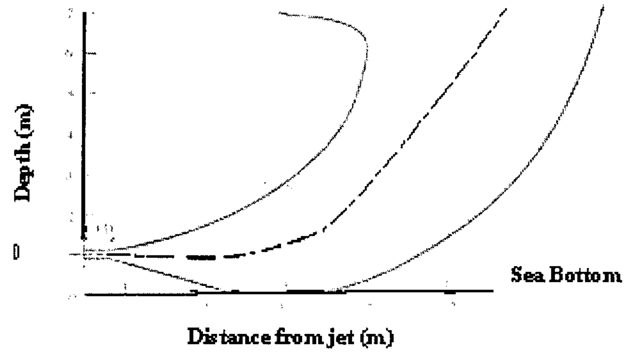


Figure 4.3 Typical horizontal discharge of effluent (source: Tsanis and Valeo, 1994)

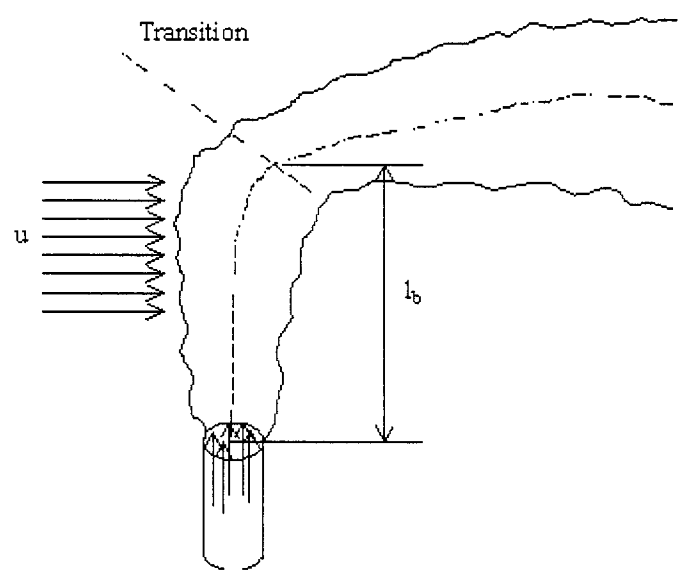


Figure 4.4 Typical vertical flows with instantaneous appearance. (source: Doneker and Jirka, 1990)

Variation of C_3 has been measured from photographic measurements in the range of 0.517 to 1.494 and 0.2254 to 1.7075 (Wright 1977a, 1977b). The constant C_4 can also be predicted from a relationship presented by (Wright, 1977b)

$$C_4 = C_5 \left(\frac{l_b}{l_m} \right)^{1/4} \qquad (4.19)$$

$$l_m = \frac{(u_j Q)^{1/2}}{u} \qquad (4.20)$$

where,

l_m = Length scale (m), a measure for momentum dominated jet with a cross flow

u_j = Initial jet velocity (m/s)

C_5 = A constant that depends on the method of obtaining data, i.e. 0.6037 from photographic and 1.2761 from concentration measurement.

C_3 and C_4 were suggested by Doneker and Jirka (1990) as 0.5824 and 1.0 respectively. For smooth transition between the *BDNF* and *BDFF*, the distance was defined by Huang et al. (1996) as

$$x_{btrans} = a_1 x_{b1} + a_2 x_{b2} \qquad (4.21)$$

where,

a_1 and a_2 = Constants

a_1 and a_2 were determined by Huang et al. (1996) as

$$a_1 = 0.5 - 0.5\,ln(z / l_b) \qquad (4.22)$$

$$a_2 = 0.5 + 0.5\,ln(z / l_b) \qquad (4.23)$$

In the *BDN*F, the rising buoyant plume is weakly deflected by the ambient water velocity. It approaches the surface almost vertically. The bulk dilution at the end of the control volume is defined by Wright et al. (1991); Doneker and Jirka, (1990); Huang et al. (1996) for *BDNF* and *BDFF* as

$$S_{a1} = C_{s1} S \qquad (4.24)$$

$$S_{a2} = C_{s2} S \qquad (4.25)$$

where,

C_{s1} and C_{s2} = Experimental constants.

C_{s1} varies from 3 to 5 in stagnant water (Wright et al. 1991; Huang et al. 1996). To incorporate the uncertainty, values between 3 and 5 are used for C_{s1} in equation 4.24 (Mukhtasor, 2001)

For the *BDFF*, the buoyant jet is strongly deflected and the approach of the buoyant jet is almost horizontal. C_{s2} was calculated from experiments to be in the range of 1.5 to 2.0 (Doneker and Jirka, 1990; Huang et al. 1996). Typical calibrated values based on field tests for the coefficients are 2.01 and 1.74 respectively (Huang et al. 1996).

The plume width at the downstream end of the control volume L_o is estimated by (Doneker and Jirka, 1990) and Huang et al. (1996) as

$$L_o = 5.2L_s \qquad \text{For } BDNF\ (z/l_b < 0.1) \qquad (4.26)$$

In this case, the upstream intrusion length, L_s was defined by Akar and Jirka (1994) and Doneker and Jirka (1990) as

$$L_s = 2.12 z^{3/2}(1-\cos\theta)^{3/2} l_b^{-1/3} \qquad \text{for } l_b/z > 6.11(1-\cos\theta) \qquad (4.27)$$

$$L_s = 0.38 l_b \qquad \text{for } l_b/z \leq 6.11(1-\cos\theta) \qquad (4.28)$$

where,

$$\theta = \tan^{-1}\left(\frac{z}{x_b}\right) \qquad (4.29)$$

is the angle between the rising jet axis and water surface as defined by Huang et al. (1996).

For *BDFF* ($z/l_b > 10$) the plume width at the downstream end of the control volume L_O is defined by the following equations with the assumption of an equivalent cross-section aspect ratio for the flow section of 2:1 (Doneker and Jirka, 1990; Huang et al. 1996).

$$L_O = 2\sqrt{\frac{S_a Q}{2u}} \qquad (4.30)$$

$$L_s = \frac{1}{sin\theta}\sqrt{\frac{S_a Q}{\pi u}} \qquad (4.31)$$

The distance from the boil center to the downstream end of the control volume is given by

$$x_{D1} = C_{D1} z \qquad \text{for } z/lb < 0.1 \qquad (4.32)$$

$$x_{D2} = C_{D2} z \qquad \text{for } z/lb > 10 \qquad (4.33)$$

where,

x_{D1}, x_{D2} = Distances of the control volume end from boil center (m)

C_{D1}, C_{D2} =Constants that have been set as 3.0 (Huang et al. 1996, Wright et al. 1991) and 0.6 (Huang et al., 1996; Doneker and Jirka, 1990).

In all cases, the plume thickness at the end of control volume can be defined by Huang et al. (1996) as

$$h_O = \frac{S_a Q}{u L_O} \qquad (4.34)$$

For the regions of $z/l_b < 0.1$ and $z/l_b > 10$, the above equations are satisfied. For the transition region, i.e. $0.1 \leq z/l_b \leq 10$, the smooth curve can be obtained using the interpolation suggested by Huang et al. (1996) as equations 4.21 to 4.23.

4.2.1 Dilution model selection

From the review of several initial dilution models, the model developed by Mukhtasor (2001) predicts dilution more realistically when compared with the others and the coefficients of the models were predicted with good statistical agreement. The prediction of dilution with a continuous equation for the *BDNF*, transition zone and *BDFF* provides simplicity in calculations. Moreover, the fit of the equation has better statistical agreement with the data than the other models (Mukhtasor, 2001). The method of predicting the constants b_3 and d_2 (Equation 4.11) is repeatable rather than the trial and error approach of Huang et al. (1998). Despite some limitations of the empirical formulation, these models can be used for predicting outfall dilution (Mukhtasor, 2001) and hence these can be employed in predicting dilution for produced water discharge.

4.2.2 Selected model's parameters

For the model (Mukhtasor, 2001), the required parameters are discussed briefly in this section.

- **Effluent discharge rate (*Q*)**

The average discharge of produced water from one platform is about 0.01736 m^3/sec (GESAMP, 1993). A study from 30 oilfields shows the range of produced water discharge to be 3.68×10^{-6} m^3/sec to 0.276 m^3/sec (USEPA, 1993). A detailed survey on produced water discharge rate has been conducted in chapter 2.

- **Height above discharge** (z)

The depth of ambient water varies between 2.5 m (Meinhold et al. 1996) to 150 m (Brandsma and Smith, 1996) at the discharge point depending on the location and type of platform. In the Open bay in Louisiana, the depth above the discharge varies from 1.3 to 5.0 meters while in the Bass Strait, the depth above discharge port is approximately 12 meters (Meinhold et al. 1996; Brandsma and Smith, 1996). Height above discharge is highly variable and is the most dominant factor in predicting dilution (Equations 4.12 and 4.13).

- **Ambient water velocity** (u)

Ambient water velocity at the offshore platform location varies between 0.03 and 0.3 m/s (Brandsma and Smith, 1996; Somerville et al. (1987)). The USEPA (1995b) used an ambient velocity of 0.05 m/sec for the open bay in Louisiana.

- **Ambient water density** (ρ_a)

The ambient water density ranges between 1005 kg/m^3 (USEPA, 1995a) to 1027 kg/m^3 (Brandsma and Smith, 1996; Somerville et al. 1987.

- **Produced Water density** (ρ_e)

Produced water density ranges between 988 kg/m^3 (Brandsma and Smith, 1996; Somerville et al. 1987) to 1140 kg/m^3 (Tibbetts et al. 1992). The data was compiled from different sources in the literature and is discussed in chapter 2.

The dilution is directly proportional to the square of the discharge depth while the discharge rate is inversely related to the dilution. Typical modeled dilution with discharge depth for an assumed flow is presented in Figure 4.5. The plume width and thickness vary with distance from the discharge port. For a typical discharge, this variation is presented in Figure 4.6. The dilution increases with the distance from the port of discharge while the plume thickness reduces sharply after its impingement with the surface water and then the rate of decrease becomes less (Figure 4.6).

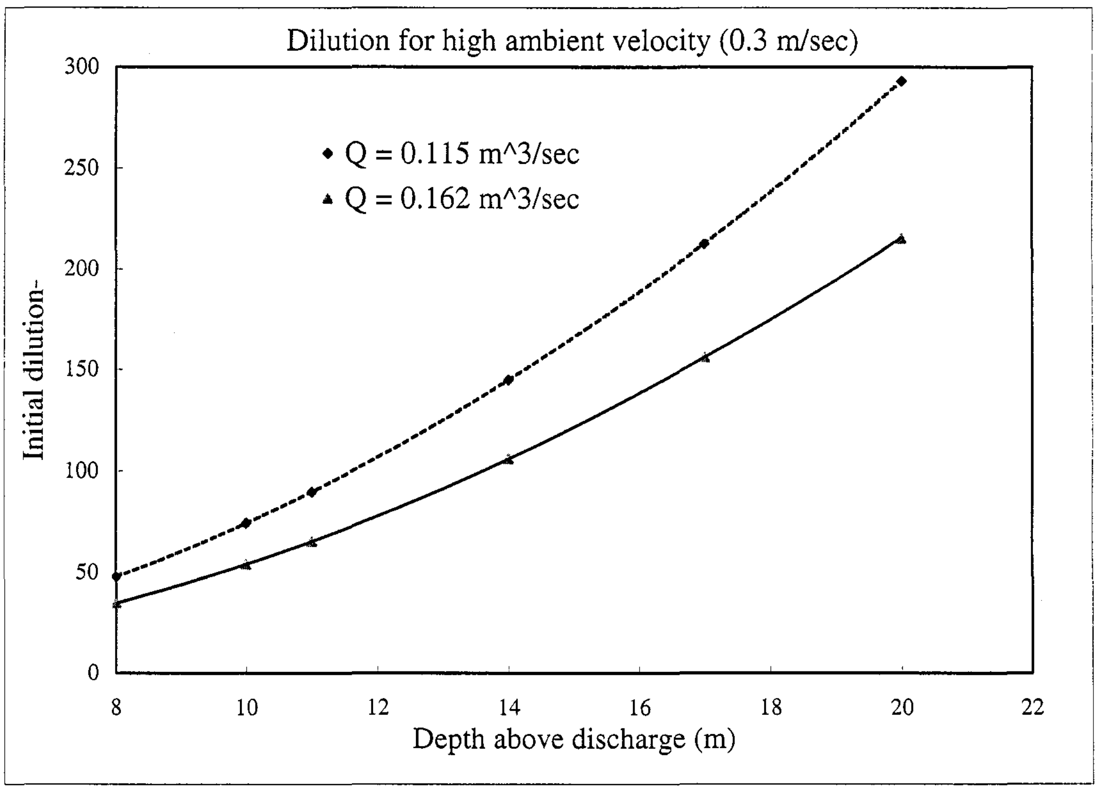


Figure 4.5 Typical dilutions with discharge depth

4.2.3 Integration of initial dilution models with dispersion models

A typical example of buoyant spreading is presented in Figure 4.7 (source: Doneker and Jirka, 1990). The dilution and dispersion of the outfall plumes are governed by the ambient flow characteristics (Huang et al. 1996) and the boundary layer of the spreading plume entrains ambient fluids (Doneker and Jirka, 1990). Turbulent diffusion and wave effects were neglected for the buoyant spreading model. Huang et al. (1996) and Mukhtasor (2001) used the buoyant spreading model that was presented by Doneker and Jirka (1990) as

$$\frac{h(x)}{h_o} = \left(\frac{L(x)}{L_0}\right)^{\alpha-1} \qquad (4.35)$$

$$\frac{L(x)}{L_o} = \left(3\beta\left[\frac{l_b}{L_0}\right]^{1/2}\frac{x}{L_0}+1\right)^{2/3} \qquad (4.36)$$

where, α is the entrainment coefficient ranging from 0.15 to 0.6. A typical field test value of α is 0.59 (Huang et al. 1996; Doneker and Jirka, 1990) and β is the model constant ranging from 0.707 to 1.414 with a typical field test calibrated value of 1.33 (Huang et al. 1996; Doneker and Jirka, 1990), l_b is the buoyancy length scale, typically evaluated at 5 m depth (Hazen and Sawyer, 1994), x is the plume centerline distance and $x = 0$ is set at the center of the downstream end of the control volume, and $L(x)$ is the plume width.

The parameter $L(x)$ is assumed to be related to $\sigma(x)$, the standard deviation of the concentration distribution across the plume width by

$$L(x) = 2(3)^{1/2}\sigma(x) \qquad (4.37)$$

The above equation is consistent with Brooks (1960). The dilution of a contaminant concentration associated with buoyant spreading processes is typically estimated by considering the error function for distribution across the plume width in the surface plume and a uniform distribution across the plume thickness (Mukhtasor, 2001). To simplify the problem, the assumption of uniform distribution of contaminants across the plume thickness has been made (Huang et al. 1996).

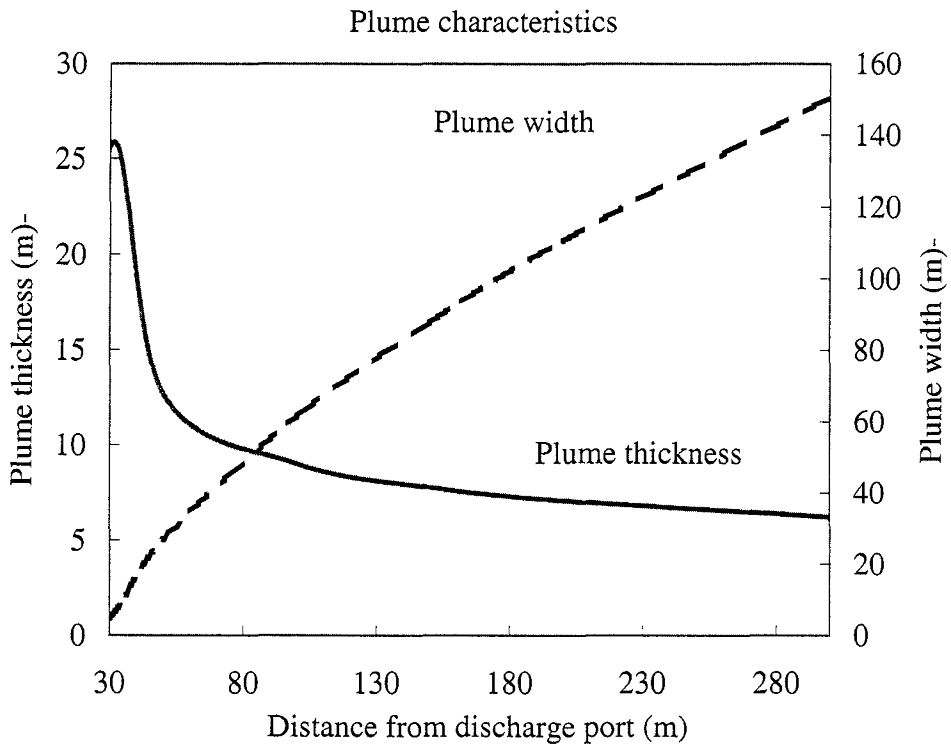


Figure 4.6 Typical variation of plume width and thickness with distance

Based on the above assumption and mass balance, the pollutant concentration at any point (x, y) is estimated (Huang et al. 1996) as

$$C(x,y) = 1.832 C_a \frac{h_o}{h(x)} \frac{1}{2} \left[erf\left(\frac{0.273 L_o + y}{\sqrt{2} \times \sigma(x)} \right) + erf\left(\frac{0.273 L_o - y}{\sqrt{2} \times \sigma(x)} \right) \right] \qquad (4.38)$$

Equation (4.38) is valid for $x \geq 0$.

where,

y = Perpendicular to x-axis in the same plane (x is along the plume centerline).

C_a = Bulk pollutant's concentration at the downstream end of the control volume (at $x=0$) estimated from associated bulk dilution.

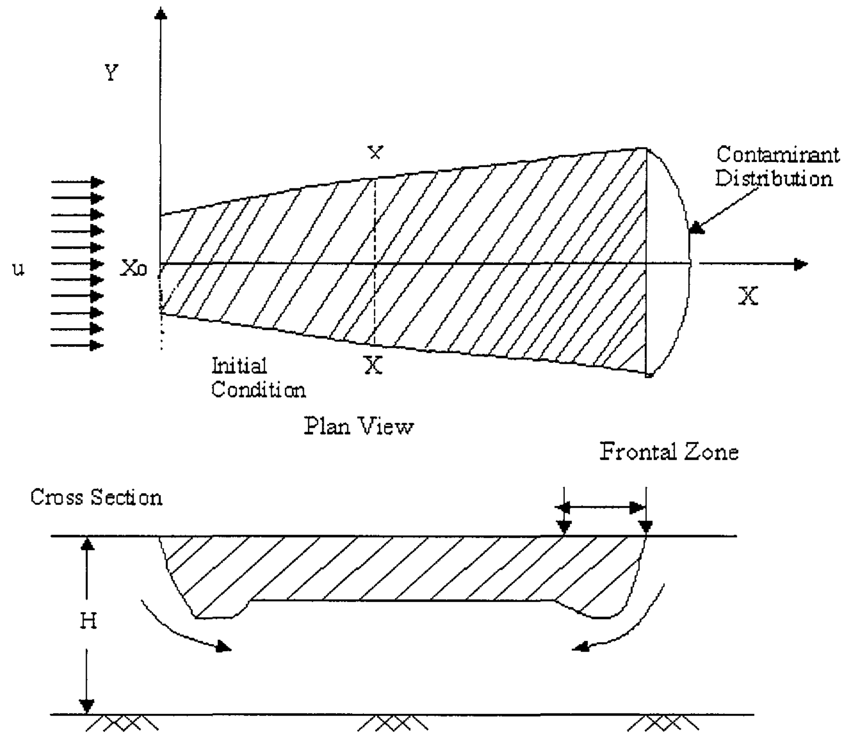


Figure 4.7 Typical buoyant spreading of outfall plume (Doneker and Jirka, 1990)

The error function can be estimated as

$$erf\,(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-z^2} dz$$

$$= \frac{2}{\sqrt{\pi}} \left(z - \frac{z^3}{3.1!} + \frac{z^5}{5.2!} - \frac{z^7}{7.3!} + \ldots\ldots \right) \qquad (4.39)$$

$$= \frac{2}{\sqrt{\pi}} \sum_{n=0}^{\alpha} (-1)^n \frac{z^{2n+1}}{(2n+1)n!}$$

The limiting values of error functions are erf (0) = 0 and erf (∞) = 1

The distribution of the related error has been assumed as normal. It such cases, the area under the normal distribution curve can be evaluated using statistical tables by a change in variable accordingly. (William,1985). The variable can be modified as

$$erf(z) = 2A(P) \qquad (4.40)$$

where,

$P = 1.414\, z$ and $A(P)$ = the area under standard normal distribution from 0 to p along the abscissa.

Equation (4.38) is valid for only $x \geq 0$. Integration of concentration distribution in the control volume zone with equation (4.38) is required and to use the equation at $x < 0$ it needs modification. At $x < (-L_s - x_D)$, it is assumed that the pollutant's concentration is zero. When $(L_s - x_D) < x < 0$, the concentration is $1.2C_a$ to be consistent with Huang et al. (1996). The average boil concentration is defined as $(C_0 / 1.7S)$ at $(-L_s - x_D) \leq x \leq (L_s - x_D)$, where C_0 is the concentration prior to the discharge and S is the centerline initial dilution (Hazen and Sawyer, 1994; William, 1985). A parabolic shaped function defined by Akar and Jirka, (1994) has been adopted for this model.

For $(-L_s - x_D) < x < 0$, the function is given by

$$L(x) = L_o \left(\frac{x + x_D + L_s}{x_D + L_s} \right)^{0.5} \qquad (4.41)$$

This model is intended to estimate hydrodynamic characteristics of the plume in the vicinity of the discharges, in which effects from turbulent diffusion are less dominant than those of buoyant spreading. Studies show that the ecological effects from produced water can generally be associated with the distance from the outfall and that the effects are usually limited to close to the discharge location (within 500m to 1000m radii) Mukhtasor, (2001). Rapid dilution in the marine environmental system may be the reason for reduced ecological impacts (Frost et al. 1998; Somerville et al. 1987; Stromgren et al. 1995). The discharge scenarios are generally designed to evaluate regulatory ambient water quality criteria, those are on mixing zone concept, and are limited to 100-200m from the discharge location (Mukhtasor, 2001). A single linear limit of 300m for the mixing zone has been incorporated in many states in the USA for simplicity (USEPA, 1995), while for human health risk assessment purposes, the USEPA (1998) used a distance of 100 meter radius around the discharge port.

The initial dilution models are in deterministic and probabilistic forms based on physical principles. The dispersion models are based on a deterministic approach with statistical error distribution. Due to the ocean characteristics and advection of the plume, the concentration of pollutants may vary both in time and space. Huang et al. (1996) defined a coordinate system to simulate this variation in which a fixed global system (*X*, *Y*) is defined and the origin is fixed at the point of discharge. A translating coordinate system (*x*, *y*) for the surface plume is defined at $x = 0$ at the end of control volume and *y* is perpendicular to the *x*-axis. The transformation between the systems is presented according to Huang et al (1996) as follows.

$$x = X\cos\varphi + Y\sin\varphi - x_b - x_D \qquad (4.42)$$

$$y = Y\cos\varphi - X\sin\varphi \qquad (4.43)$$

where,

φ =Current direction (radian) with respect to the X - coordinate direction.

X and Y are the global axes with origin *(0,0)* at the point of discharge. X is in the ambient current's direction and Y is perpendicular to the X-axis.

The simulated concentration may be considered as a "snapshot" of an outfall plume at a particular time and space. The configuration and motion of plumes are then simulated by a series of "snapshots". The area of selection can be divided into uniform grids and by employing near, intermediate and far field models can estimate the concentration at each grid. A typical grid for the control volume is presented in Figure 4.8. For a hypothetical offshore oil field in eastern Canada having a discharge of 0.212 m^3/sec with the port at 12m depth from the surface without any stratification, a contour was plotted for a 300m × 300m zone. A typical plot is shown in Figure 4.9. The ambient density was assumed as 1025 kg/m^3 and the produced water density as 1005 kg/m^3. A comparison of dilution in the near field region (*NFR*) using the CORMIX model and the Mukhtasor (2001) model is shown in Table 4.1.

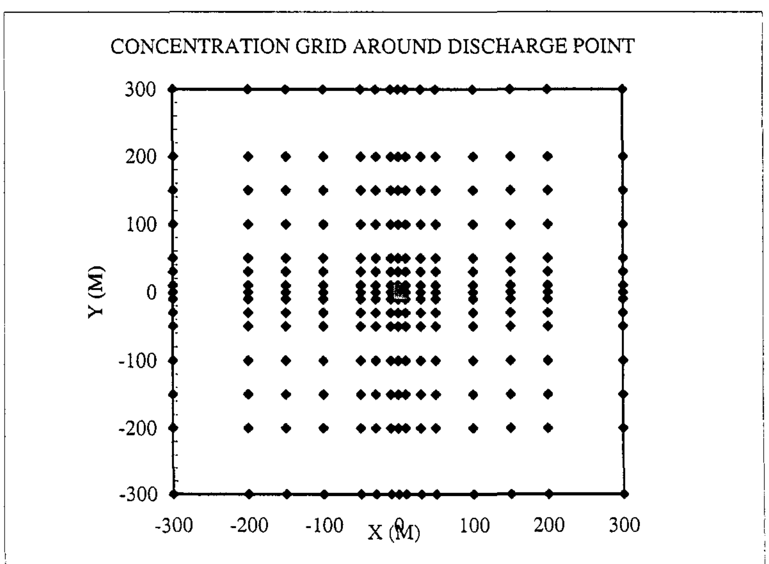


Figure 4.8 Concentration grids around the discharge point

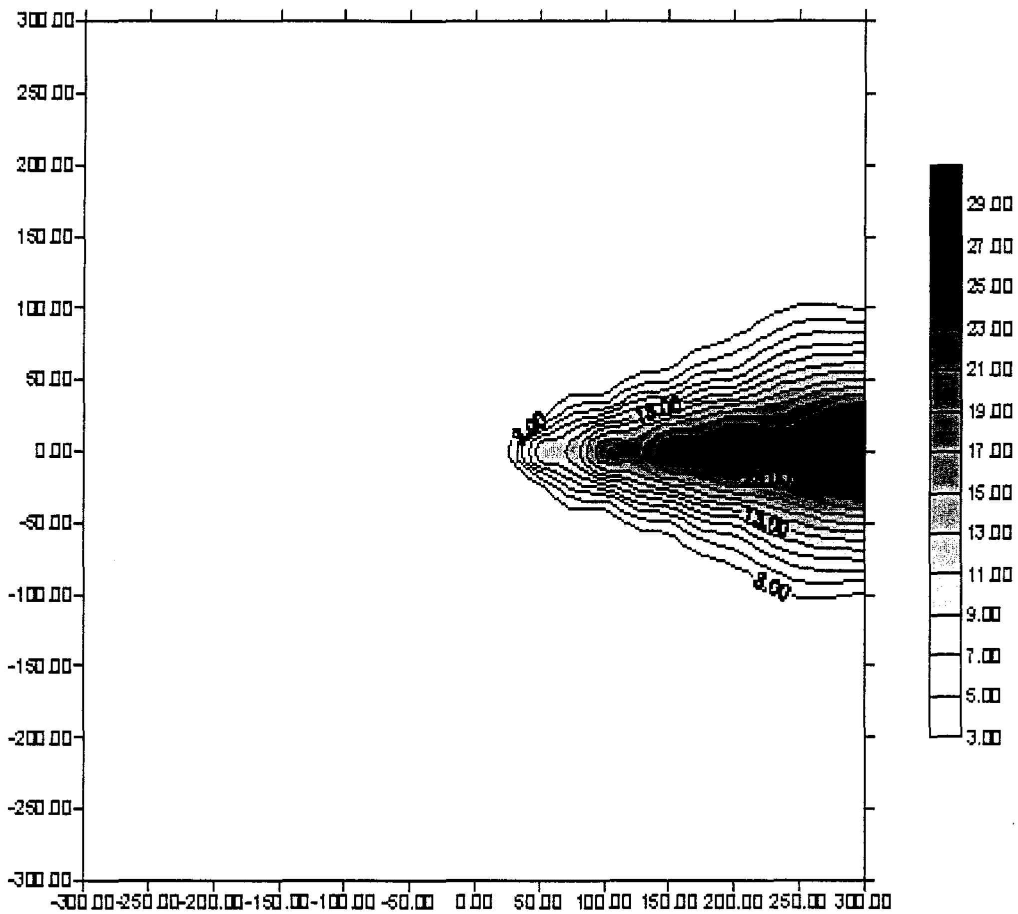


Figure 4.9 Typical contour for produced water plume.

Table 4.1 Dilution comparisons with CORMIX model

Scenario	Dilution by Mukhtasor (2001) model	Dilution by CORMIX Model	
		Without surface wind	With surface wind
Q=0.212 m^3/sec; u = 0.06 m/sec ρ_a=1026 kg/m3; ρ_e=988 kg/m3 z =11m	26.3	24.4	34.7
Q=0.212 m^3/sec; u = 0.06 m/sec ρ_a=1026 kg/m3; ρ_e=1000 kg/m3 z =11m	23.6	22.4	28.3
Q=0.212 m^3/sec; u = 0.06 m/sec ρ_a=1027 kg/m3;ρ_e=1014 kg/m3 z =11m	21.6	19.4	21.5

Mukhtasor (2001) did not consider the effects of water surface wind. The predicted dilutions by Mukhtasor's (2001) model for three different scenarios are close to the CORMIX prediction but the difference is significant if the ambient wind is considered (Table 4.1).

4.2.4 Integration of models with contaminants database

The selection of the contaminants is to be made from the database. The program is interfaced with an MS Access database for the contaminants in produced water that have been stored in the system. Upon selection of a contaminant, the contaminant is activated and an automatic link is developed within the software system. Based on the input parameters, the software calculates the concentration of the contaminant in the ambient seawater. The initial dilution models and the related components (Equations 4.12 to 4.43) have been connected sequentially in the software system. The inter-relations of the database with the models used in the package have been described in Figure 4.10. The probabilistic analysis and graphical outputs have been performed in spreadsheets, which can be accessed using a mouse click as in Figure 4.11. A user manual to use the software is provided with the software.

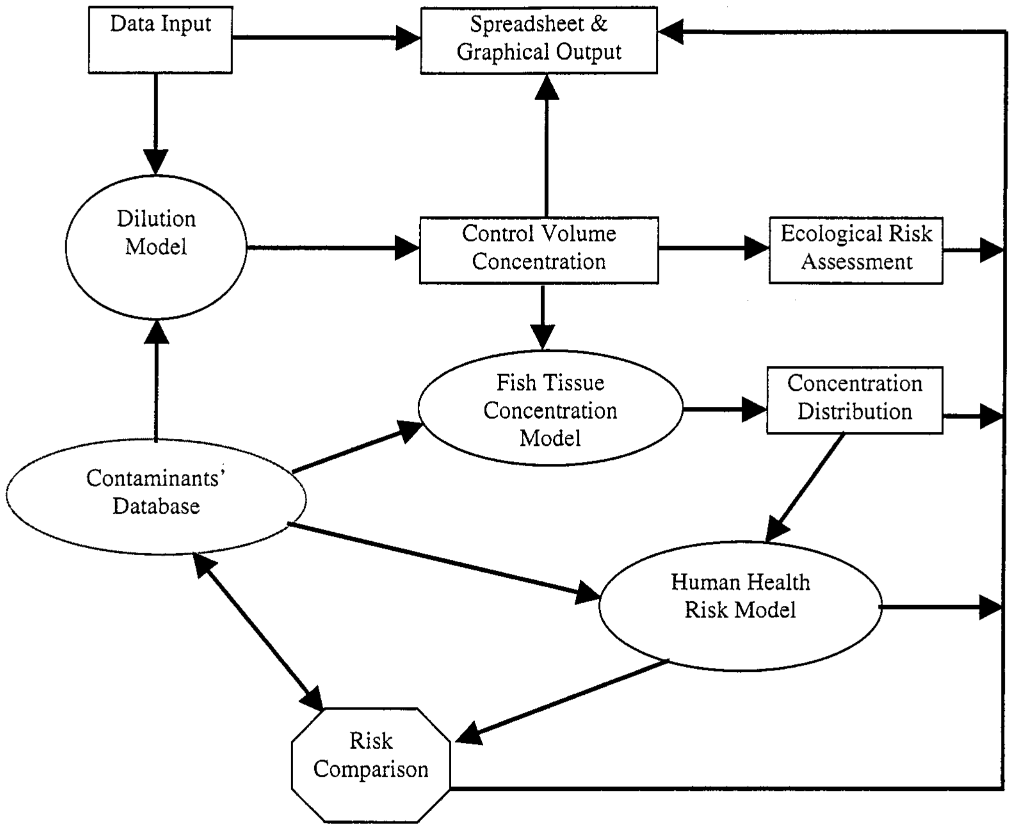


Figure 4.10 Framework of the software development

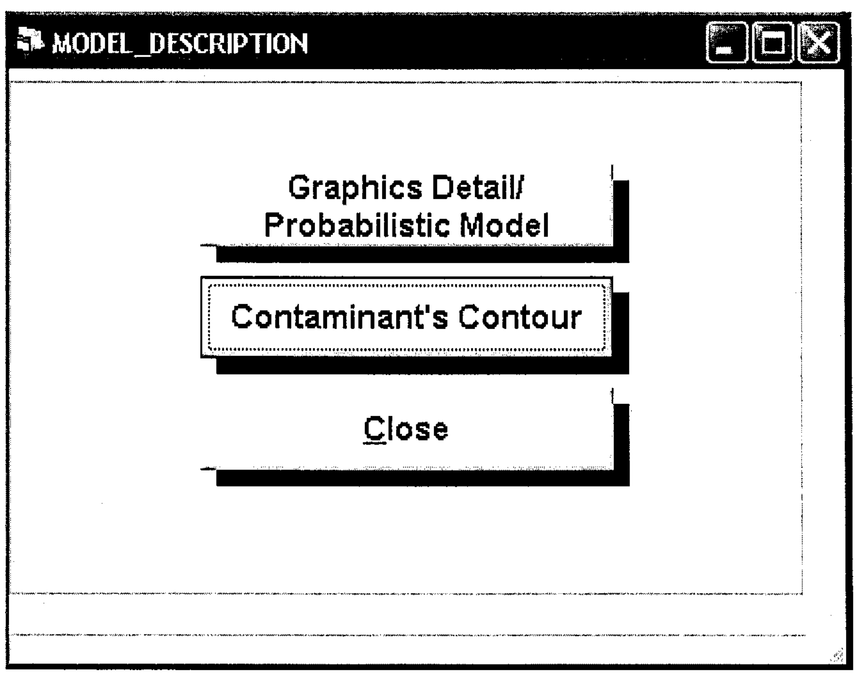


Figure 4.11 Opening interface of spreadsheet details

4.2.5 Dilution model parameters and contaminant(s) concentration input

The model parameters such as effluent discharge rate, density, depth of the discharge port from water surface, ambient water velocity and density are relevant to a given site. The concentration of the contaminant is variable with site selection. These parameters can be entered using a model input interface as shown in Figure 4.12. The Model description is available for viewing and printing. Graphical descriptions of control volume, boil location (x_b), plume's width (L_o) and thickness (h_o) at the end of control volume, plume's upstream intrusion length (L_s), z/l_b, and vertical angle of the jet (θ) are available for viewing. These are calculated by the model equations and typical figures are shown in Figure 4.13. Mukhtasor (2001), Huang et al., (1996) and Doneker and Jirka (1990) have discussed the parameters in details.

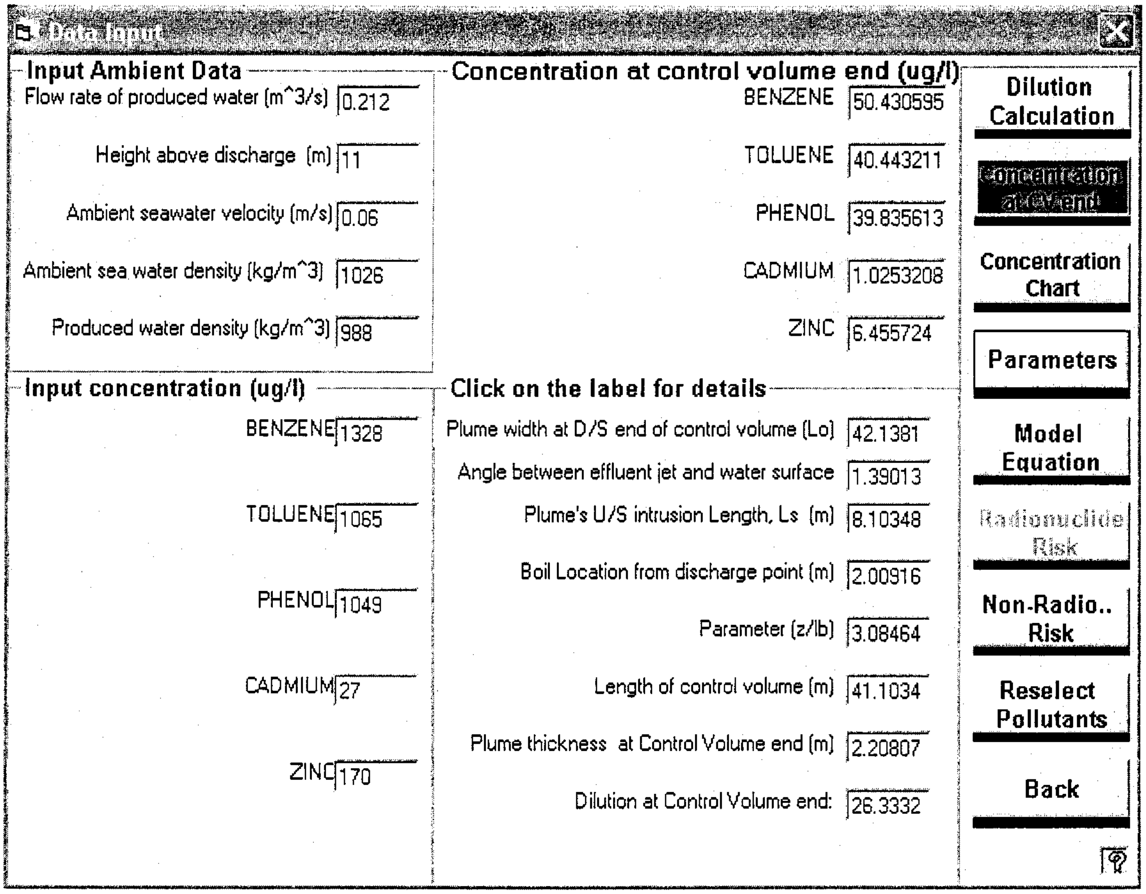
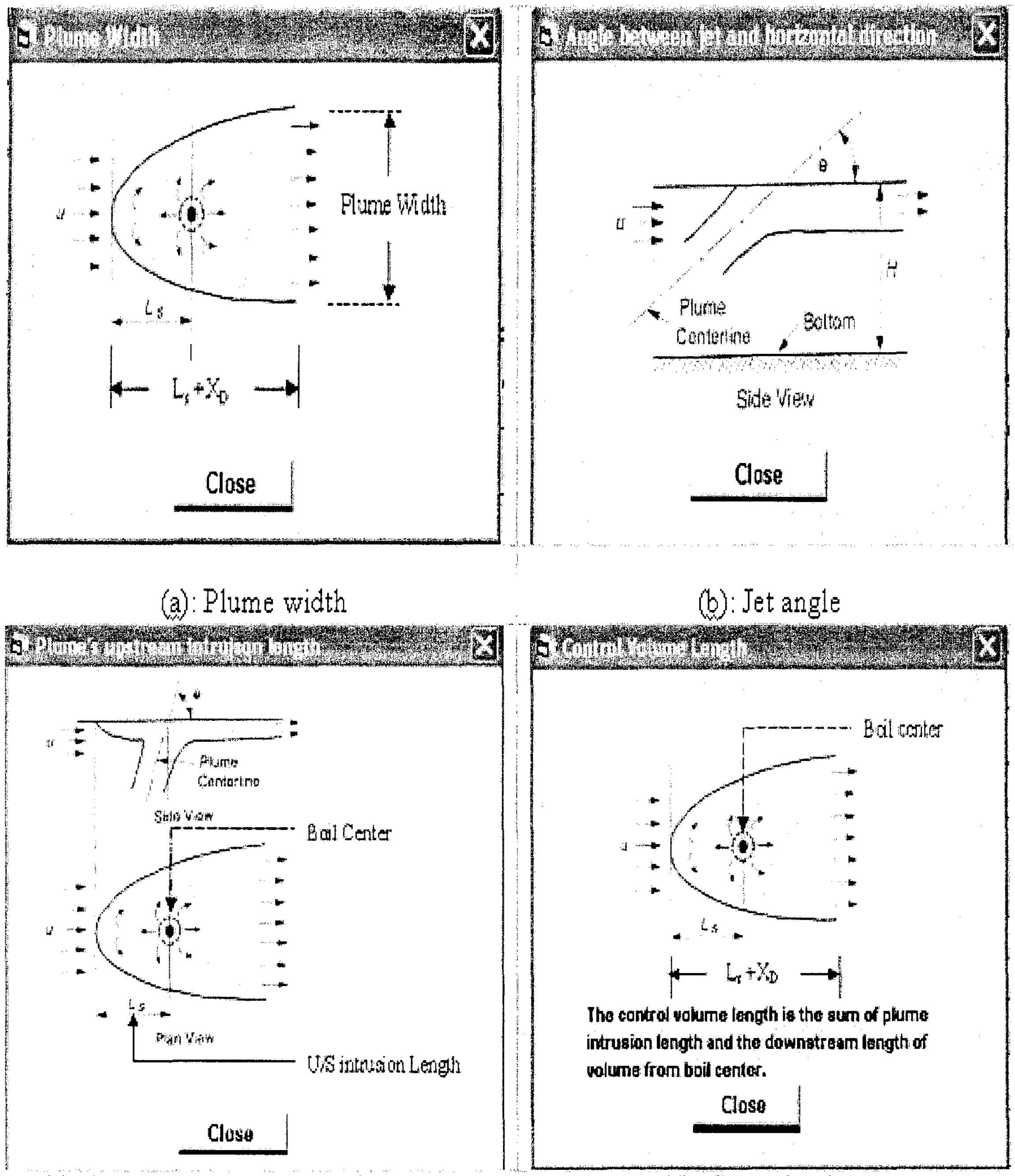


Figure 4.12 Model data and contaminant's concentration input



(a): Plume width

(b): Jet angle

(c): Plume's upstream intrusion length

(d): Control volume

Figure 4.13 The parameters for the dilution model

4.3 Integration of fish growth model with exposure concentration

The fish growth models (Equations 3.16 and 3.17) have been incorporated with the software system. Equation 3.16 predicts the total weight deterministically and equation 3.17 does the same in probabilistic form. Based on the total weight and variability in lipid contents of fish, the total amount of the accumulated contaminants in fish can be predicted. This contaminant will be analyzed for human health risk assessment purposes.

4.3.1 Fish growth model parameters

The parameters required to predict fish growth are

- Initial weight of fish (W_o)
- Parameter (a) and (c)

For an illustration, a migratory fish like Rainbow Trout (*Salmo Gairdneri*) is considered. The Rainbow Trout spawns from January to May in fresh water. During its life cycle, it spends about 1-2 year in fresh water and then migrates to the sea when it has a weight of 50-200g (Huet, 1986; Robin, 1989). At the time of spawning, it returns to the fresh water and spawns (Huet, 1986). This weight can be considered as the initial weight (W_o) of fish for the growth model. The other two parameters to predict growth of fish have been denoted by a and c. These two parameters have been predicted as 0.34 (0.32-0.36) and 1.59 (1.54-1.64) respectively in Chapter 3. An error term for the probabilistic model (equation 3.17) has been introduced as $N\,(0,0.12)$. This error term is normally distributed with a mean 0 and standard deviation 0.12.

4.4 Summary

The importance of dilution models and their methods of calculation have been discussed in this chapter. The available dilution models and their limitations have also been discussed. The advantages of dilution models by Mukhtasor, (2001) over the other available models have been described. Integration of fish growth models has been performed. The approach of the software to predict risks has been shown in this chapter. In predicting the exposure concentration (*EC*), the probability of exposure (*p*) and the bioavailability will be incorporated in the predicted environmental concentration (*PEC*) calculated in this chapter. The following chapters discuss the ecological and human health risk framework based on the predictions in this chapter.

Chapter 5.

A Methodology for Risk Assessment from Produced Water

5.1. Introduction

Risk assessment is a careful investigation for any stressor that may cause harm to a selected endpoint that has environmental or economical importance. Ecological risk assessment (*ERA*) evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors (USEPA, 1998a; CCME, 1997). In this chapter, methodologies of the ecological and human health risk associated with produced water discharges from offshore operations will be discussed.

5.2 Ecological risk from contaminants in produced water

The ecological risk assessment of produced water has gained much attention in the last two decades. Numerous studies on *ERA* have been carried out to assess the ecological risk from produced water (Brendehaug et al. 1992; Stagg et al. 1996; Neff et al. 1979;

Neff and Sauer, 1996; Neff et al. 1997; Neff, 2002; Booman and Foyn, 1996). Considerable research has been conducted in characterizing ecological risks from produced water contaminants (Ray and Engelhardt, 1992; Reed and Johnsen, 1996). Addressing the ecological impacts, several regulatory agencies set different discharge criteria for the oil content of produced water in different regions (C-NOPB, USEPA, MMS, OSPAR).

No significant biological effects from chronic exposure to produced water to a caged fish were detected in a study by the OGP (2002). 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 toxicity by Holdway (2002) and Neff (2002) as a percent of total oil in produced water. Neff et al. (1996) concluded, that the risk from *PAHs* in produced water was minimal. In that study, the concentrations in ambient water, sediment and fish tissue were compared with threshold limits. 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 a 5-day exposure, effects on oxygen consumption were detected at 25 μg/l and 100 μg/l concentrations (Booman and Foyn, 1996). Booman and Foyn (1996) determined the 24-hour LC_{50} as 7 mg/l *BTX* (mixture of benzene, toluene and xylene) 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 thus volatile components fall below the criteria limit within a short distance from the discharge point (Neff and Sauer, 1996). Karman et al. (1996) performed a quantitative risk assessment for the Statfjord and Gullfaks oil fields. In that assessment, the predicted environmental concentration (*PEC*) was divided by the predicted no-effect concentration (*PNEC*) to determine ecotoxicological risk. *PNEC* is the highest concentration at which almost all biota are protected. The *PNEC* was calculated as

$$PNEC = \frac{GM}{1000/\sqrt{n}} \qquad (5.1)$$

where,

PNEC = Predicted no-effect concentration

GM= Geometric mean of all available EC_{50} or LC_{50} values. However to be more conservative, *NOEC* for the most sensitive effect parameters is considered if data is available (Mukhtasor, 2001)

n = Number of species for which toxicity data for that chemical is available

5.3 Framework for ecological risk assessment

The comprehensive framework for ecological risk assessment (*ERA*), developed by the USEPA (1998a) is presented in Figure 5.1. The risk assessment framework has three main components as

- Problem formulation
- Analysis
- Risk characterization

5.3.1 Problem formulation

Problem formulation is the foundation and first step of the entire ecological risk assessment. It is a process of describing the sources of stressors, identifying the endpoints and the reasons for endpoints being affected. The entire process consists of three components: (i) assessment endpoints (ii) conceptual models and (iii) analysis plan.

Assessment endpoints are critical to problem formulation as these should be the explicit expressions of actual environmental value that is to be protected. Three principle criteria are used to select assessment endpoints: (i) ecological relevance, (ii) susceptibility to potential stressors and (iii) relevance to the management goals. Fish has been assumed as the main assessment endpoints by several regulatory agencies and researchers (ANWQG, 2000; Mukhtasor, 2001; Sadiq, 2001; USEPA ECOTOX online database).

The conceptual models are presented to express the relationship between ecological entities and stressors. Produced water may affect the benthos because of contaminants' accumulation in the sediments, but such impacts may be difficult to detect due to natural spatial and temporal variability in population density of infaunal organisms (Osenberg et al. 1992). Higashi et al. (1992) observed that the water-soluble fraction in produced water from a Carpinteria, California platform has the most biological effects while the sediments adsorbed fraction has the least effects. The egg, larvae, small fish and other small organisms drift with the water column and thus are exposed to the produced water plume. The larger fish move throughout the water column, eat phytoplankton, zooplankton and smaller fish and thereby are exposed through contact and the food web.

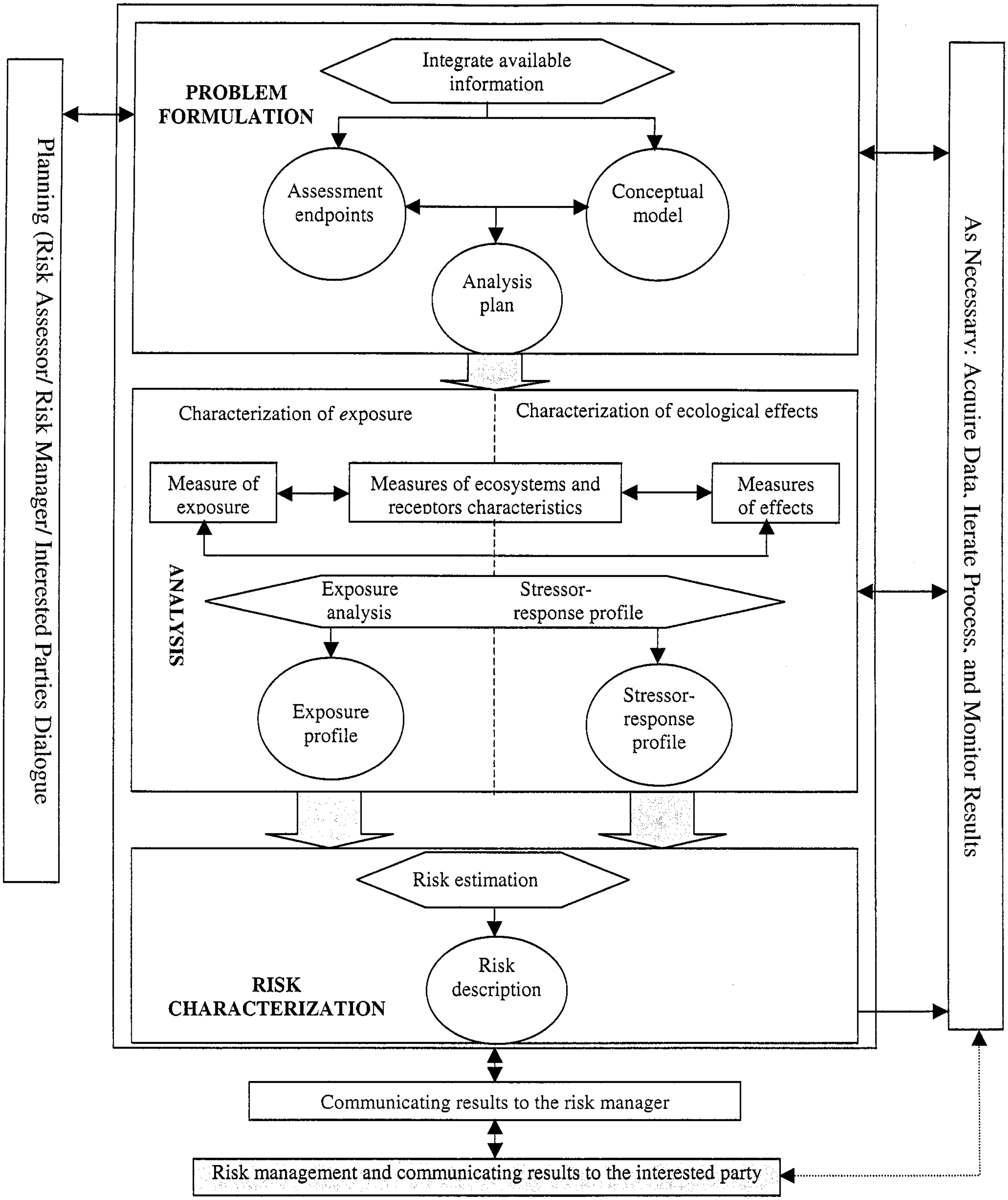


Figure 5.1 Framework for ecological risk assessment (USEPA, 1998a)

The analysis plan is the final component in problem formulation, which includes the methods, data needs, and methods of performing analysis phase. This component includes pathways and relationships identified during problem formulation that will be pursued during the analysis phase.

5.3.2 Analysis phase

Analysis is a process that identifies the two primary components of risk, exposure and effects, and the relationships between each other and ecosystem characteristics. There are three steps to be followed in the analysis phase.

- Evaluating the validity of data and models to be used for the analysis phase
- Characterization of exposure
- Characterization of ecological effects

Evaluating the validity of data and models has been discussed in chapter 2 to 4.

Characterization of exposure identifies the sources of contaminants, their exposure pathways and describes their temporal and spatial distribution. The source of contaminants is the first and most important component in the exposure analysis. The source can be defined in two ways. The first is the location where the stressors originate. In case of produced water discharges, the outlet point of the pipe is the original source. The second source can be defined as the current location of the stressors. The contaminants, which are transported from discharge port to the water column due to momentum, buoyancy and ambient current, could be the future source of contaminants.

The source characterization should consider the influence of the emission on transport, transformation or bioavailability of the stressor.

Bioavailability of the stressors is the extent to which a contaminant can be absorbed by a living organism. Although the solubility of PAHs and other organics vary widely, to be in conservative prediction, all contaminants except metals have been assumed as completely dissolved in produced water and thus are 100% bioavailable to the marine organisms. The terms, leaching factor (*LF*) and conversion factor (*CF*) were incorporated to determine the bioavailable fraction of heavy metals in the pore water of sediments for drilling waste discharges (USEPA, 1996; USEPA, 2000). Table 5.1 presents a partial listing of leaching factors and conversion factors of some metals. The conversion factors were derived assuming a hardness of 100 mg/l as $CaCO_3$ (USEPA, 1996). The predicted environmental concentration (*PEC*) of the contaminant is adjusted by multiplying *PEC* with a factor for bioavailable fraction.

Table 5.1 Factors to determine bioavailable fraction of contaminants

Metals	Leaching factor (*LF*)	Conversion factor (*CF*) for saltwater
Arsenic	0.005	1.000
Cadmium	0.11	0.994
Chromium (III)		N/A
Chromium (IV)	0.034	0.993
Copper	0.0063	0.83
Lead	0.02	0.951
Mercury	0.018	0.85
Nickel	0.043	0.99
Selenium	--	0.998
Silver	---	0.85
Zinc	0.0041	0.946
Iron	0.13	---
Barium	0.0021	---

The next important component is the spatial and temporal distributions of the stressors, which is predicted in this research by the dilution and dispersion models. The migratory organisms including fish need not stay close to the contaminated plume and the organism can move within the area under study. The probability of exposure (p) was determined as the ratio of the impact zone to the area under study (USEPA, 2000; Sadiq 2001). The USEPA (1999) used an area of 100m radius around the point of discharge for predicting human health risk. A similar approach for this study has been followed to predict probability of exposure (p). The exposure concentration is adjusted as

$$C_{exp}=C_w \times p \times BAF \qquad (5.2)$$

where,

C_{exp} = Exposure concentration for fish

C_w = Predicted Environmental Concentration (PEC). It is predicted using equations 4.12, 4.13 and 4.38

p = Exposure probability

BAF = Bioavailable fraction

Determination of the contact or co-occurrence of the stressors and the endpoints is the final step in exposure assessment. For produced water, the contact of marine organisms is quantified as the amount of contaminants ingested, inhaled or absorbed through skin. Internal absorption for some stressors is also required to determine actual contact and the uptake is evaluated by considering the amount of contaminants internally absorbed by an organism. For conservativeness and simplicity, the internal absorption for all contaminants except radionuclides has been assumed to be 100 percent in this research.

The gastrointestinal absorption factors for radionuclides from USEPA (1999a) have been used in this study.

Characterization of ecological effects describes the effects induced by a stressor, links them to the assessment endpoints and evaluates the changes with varying stressor level (USEPA, 1998a). The effects from produced water discharges can be acute or chronic. The effects resulting from a shorter exposure (96-hour or less) is called as an acute effect (USEPA, 1991). The acute effects are of different types including respiration effects, death, food intake. The effect that is carried out for a long time, such as several years or even throughout one-tenth or more of a life span, is known as a chronic effect. The chronic effects are characterized as reduced growth, reduced reproduction and change in lifecycle including lethal effects (USEPA, 1991). The primary focus of ecological risk assessment is the individual organism as it has optimum organizational characteristics, which can be studied easily (Suter, 1993; Calabrese and Baldwin, 1993; Osenberg et al., 1992). The toxicological information of individual contaminants in produced water has been compared with the exposure concentration (*EC*).

5.3.3 Risk characterization

Risk characterization is the final phase of ecological risk assessment (*ERA*) and describes the adverse ecological effects to the selected end points. The associated uncertainties in the models are also discussed in this phase. The ratio of exposure concentration to the concentration that causes effects is the quotient. For a mixture of chemicals, the hazard quotient for each constituent for certain toxicity endpoints (e.g.,

LC_{10}, LC_{50}, EC_{10}, EC_{50}, *NOEC*, etc) are calculated and added together assuming the toxicities are additive or approximately additive; but the toxicity of a chemical mixture may be greater or less than the predicted individual toxicities and thus additive toxicity may result in erroneous conclusion (USEPA, 1998a; USDOE, 1998). Table 5.2 presents toxic effects of chemical mixtures on fish. The ratio between mean exposure concentration and *PNEC* is shown in Figure 5.2a. Uncertainties can be incorporated into single-point estimates to provide a statement of likelihood that the effect point estimate exceeds the exposure point estimate (Figures 5.2b and 5.2c). In produced water discharges, the single point estimates for exposure and effects (Figure 5.2a) and the uncertainty in exposure will be considered (Figure 5.2b). The mean response concentrations have been adopted through literature search and documented in the databases in the appendices.

Risk quantification can be performed for up to five non-radionuclide and three radionuclide contaminants in a single run. The analysis for a single chemical can also be performed in this software. The hazard quotient for each contaminant is determined as

$$HQ = \frac{\text{Exposure concentration}}{NOEC\ \text{(No observed effect concentration)}} \qquad (5.3)$$

where,

HQ = hazard quotient

Table 5.2 Responses and effects from chemicals mixture (Calabrese and Baldwin, 1993)

Toxicants	Response	Species	Joint action	Multiple of additive joint action
Ammonia + Phenol	Threshold LC_{50}	Rainbow trout	Additive	0.7 to 1.0
Ammonia + Copper	48-hr LC_{25}	Rainbow trout	More than additive	1.2
Phenol + Copper + Zinc	48-hr LC_{50}	Rainbow trout	Less than additive	0.9
Nickel + Copper + Zinc	48-hr LC_{50}	Rainbow trout	Additive	0.7
Cyanide + Chromium	30-day EC_{50} (growth)	Fathead minnow	Less than additive	0.6-0.8
Cyanide + Zinc	96-hr LC_{50}	Bluegill	Less than additive	0.4
Cadmium + Copper + Zinc	96-hr LC_{50}	Fathead minnow	More than additive	1.3
Nickel + Chromium	10-week LC_{50}		More than additive	13

The occurrence of exposure to each of the contaminants has been assumed as independent and the total risk is predicted as

$$\left.\begin{aligned}
R(A+B+C+D+E) &= R(A+B+C+D)+R(E)-R(A+B+C+D)\times R(E)\\
R(A+B+C+D) &= R(A+B+C)+R(D)-R(A+B+C)\times R(D)\\
R(A+B+C) &= R(A+B)+R(C)-R(A+B)\times R(C)\\
R(A+B) &= R(A)+R(B)-R(A)\times R(B)
\end{aligned}\right\} \quad (5.4)$$

where,

A, B, C, D and E = 1st, 2nd, 3rd 4th and 5th contaminant respectively

R refers to respective effect

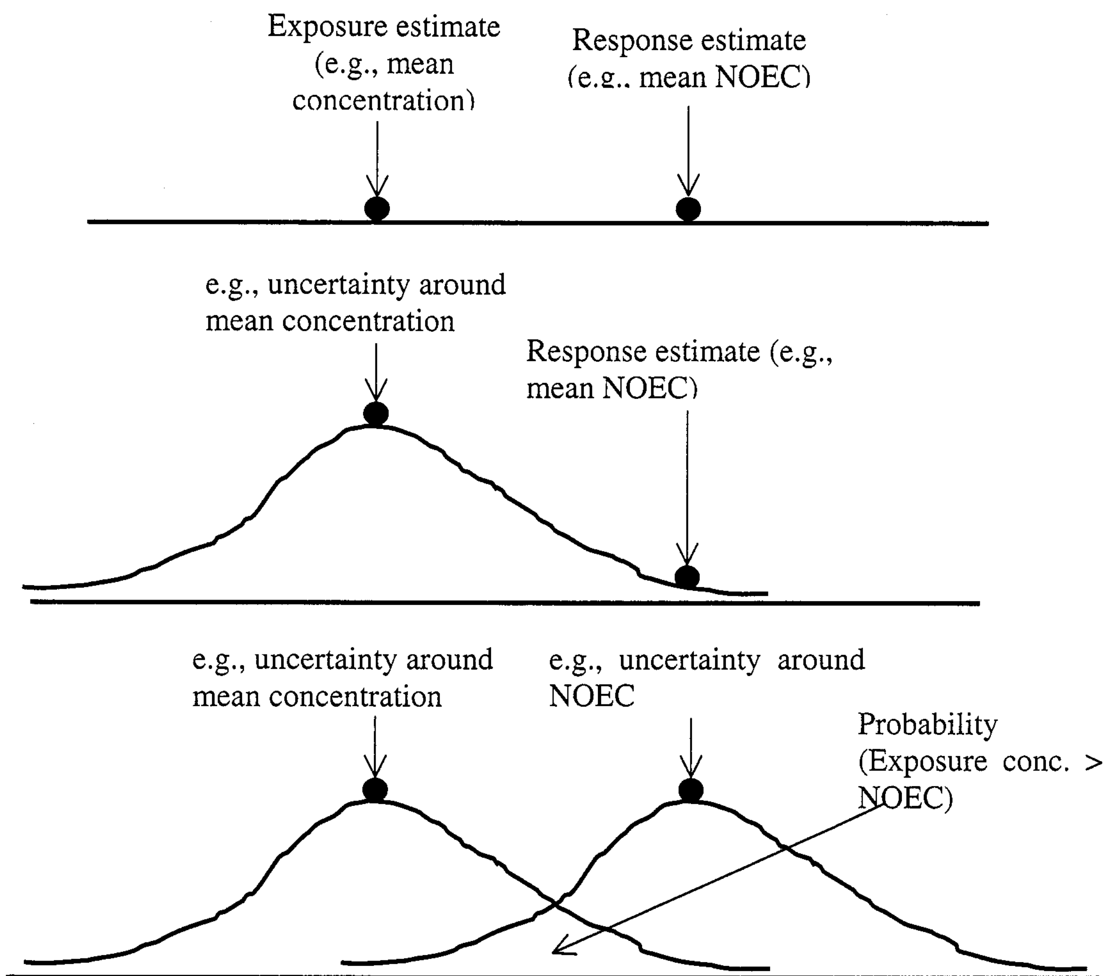


Figure 5.2 Risk estimation techniques: (a) Comparison of point estimate; (b) Comparison of point estimate of a stressor-response relationship with uncertainty associated with an exposure point estimate (c) Comparison of point estimates with associated uncertainties (source: USEPA, 1998a)

5.4 Human health risk from contaminants in produced water

Produced water discharges from offshore platforms may pose a human health risk through seafood ingestion. Study of human health risk from radium, a radioactive contaminant in produced water, has become important over the last decade (Meinhold and Hamilton, 1992; Meinhold et al. 1996; Hamilton et al. 1992). Meinhold et al. (1996) predicted elevated risk from lead ingestion in fish for produced water discharges in the Open bay, Louisiana. Certain types of contaminants discharged from offshore operations may be accumulated in fish tissues and thereby pose risk to human health through food ingestion (Sadiq, 2001; USEPA, 2000). The evaluation of a conceptual model for risk assessment purposes can be performed through justifying related hypotheses. These are tabulated in Table 5.3. For produced water discharges, the source of contaminants is produced water as described in chapter 2; the pathway is seafood ingestion that may be contaminated with toxic chemicals in produced water; and the receptors are the human beings.

Table 5.3 Conceptual model evaluation (source: USEPA, 1989a)

Component	Variables	Hypotheses to be tested
Sources	▪ Contaminants ▪ Concentrations ▪ Time ▪ Locations	▪ Source exists ▪ Source can be contained ▪ Source can be removed and disposed ▪ Source can be treated
Pathways	▪ Media ▪ Rates of migration ▪ Time ▪ Loss and gain functions	▪ Pathway exists ▪ Pathway can be interrupted ▪ Pathway can be eliminated
Receptors	▪ Types ▪ Sensitivities ▪ Time ▪ Concentrations ▪ Numbers	▪ Receptor is not impacted by migration of contaminants ▪ Receptor can be relocated ▪ Institutional controls can be applied ▪ Receptor can be protected

5.5 Prediction of fish tissue concentration

Produced water may contain radium as a part of naturally occurring radioactive material *(NORM)* in addition to other contaminants like metals, *PAHs*, *VOC* etc. Radium disintegrates through emissions of alpha, beta and gamma particles as characterized in chapter 2. A different approach for radium concentration in fish tissue has been discussed in section 5.5.1 below.

5.5.1 Fish tissue concentration for non-radionuclides

The weight of fish is predicted using the initial weight and parameters as described in section 4.3.1 in which the total lipid content can be predicted on the basis of lipid percent in a fish. Moisture and lipid content in a fish varies with species and time. These are tabulated in Table 5.4. In the Storage and Retrieval (*STORET*) database, the 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. In the National study of chemical residues in fish (*NSCRF*) report, the values range from 1.6 to 4.9 and 3.8 to 6.3 percent respectively USEPA (1992). The edible part in a fish was determined as the sum of moisture and lipid content in a fish from Table 5.4. These data reveal edible parts of a minimum of 64% and a maximum of 87% with a mean of 78% in fish. The edible parts in fish follow a lognormal (4.36,0.063) distribution. The Figure 5.3 shows the probability plot. The lipid percent of fish also follows a lognormal (1.139,1.032) distribution. The probability plot is shown in Figure 5.4. The total contaminants accumulated in fish tissue can be predicted with the respective bioconcentration factors as noted in Appendix 1. The following equations have been formulated to calculate fish tissue concentration.

$$C_L = C_{exp} \times BCF \qquad (5.5)$$

where,

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

BCF = Bioconcentration factor (l/kg)

C_{exp} = Exposure concentration (μg/l) as predicted by equation (5.2)

$$W_L = W_t \times F_L \qquad (5.6)$$

where,

W_L = Weight of lipid (kg)

W_t = Weight of fish (kg)

F_L = Fraction lipid content in a fish

The total contaminants in a fish is calculated from

$$W_c = C_L \times W_L \qquad (5.7)$$

where,

W_c = Total accumulated contaminants in a fish (μg)

By distributing the contaminants throughout the whole edible part of a fish, the tissue concentration was predicted as

$$C_f = \frac{W_c}{F_{epr} \times W_t} \qquad (5.8)$$

where,

C_f = Concentration in fish tissue (μg/kg)

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

Table 5.4 Moisture and lipid content in selected species (source: USEPA, 1996a)

Species	Moisture content (%)	Total lipid content (%)	Category	Comments
Anchovy, European	73.37	4.101	Finfish	Raw
Bass, Stripped	79.22	1.951	Finfish	Raw
Carp	76.31	4.842	Finfish	Raw
Haddock	79.92	0.489	Finfish	Raw
Halibut, Atlantic and Pacific	77.92	1.812	Finfish	Raw
Halibut, Greenland	70.27	12.164	Finfish	Raw
Herring, Atlantic & Turbot	72.05	7.909	Finfish	Raw
Herring, Pacific	71.52	12.552	Finfish	Raw
Mackerel, Atlantic	63.55	9.076	Finfish	Raw
Ocean Perch, Atlantic	78.80	1.296	Finfish	Raw
Pike, Northern	78.92	0.477	Finfish	Raw
Salmon, Atlantic	68.5	5.625	Finfish	Raw
Salmon, Chinook	73.17	9.061	Finfish	Raw
Salmon, Coho	72.63	4.908	Finfish	Raw
Salmon, Pink	76.35	2.845	Finfish	Raw
Sardine, Atlantic	59.61	10.545	Finfish	Canned in oil
Seatrout, mixed species	78.09	2.618	Finfish	Raw
Trout, Rainbow	71.48	2.883	Finfish	Raw
Trout, mixed species	71.42	5.901	Finfish	Raw
Crab, Alaska King	79.57	N/A	Shellfish	Raw
Lobster, Northern	76.03	0.358	Shellfish	Raw
Shrimp, mixed species	52.86	10.984	Shellfish	Cooked, breaded and fried
	72.56	1.421		Canned
Mussel, Blue	80.58	1.538	Shellfish	Raw
Oyster, Eastern	85.14	1.620	Shellfish	Raw
Squid	78.55	0.989	Shellfish	Raw
	64.54	6.763		Cooked, Fried

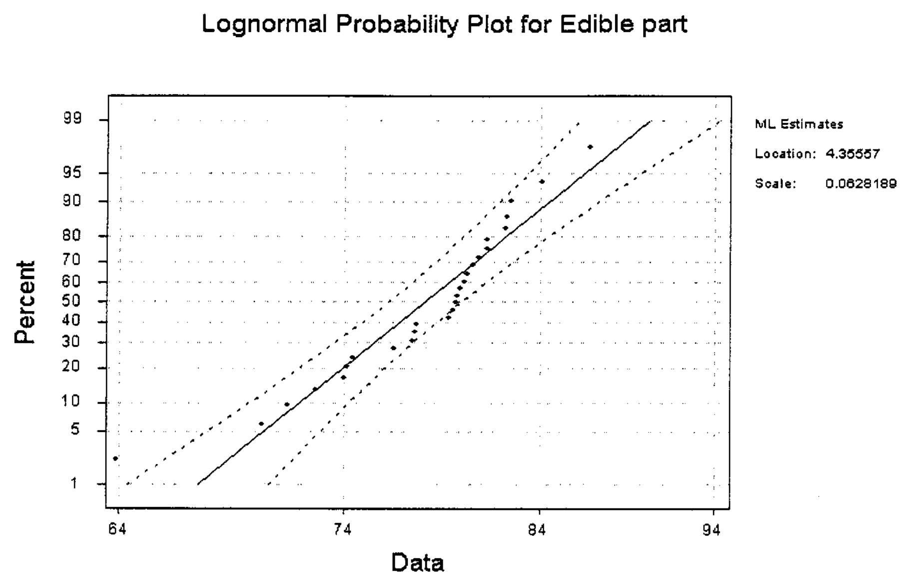


Figure 5.3 Lognormal probability of edible part in a fish

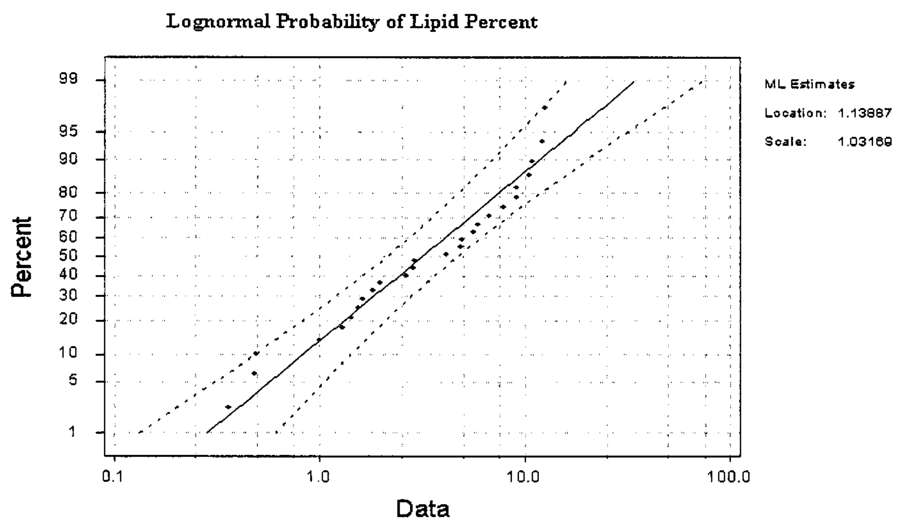


Figure 5.4 Lognormal probability of lipid percent in fish

The edible part of a fish excludes the bones, gills, guts and the external part of the skin. In Table 5.4, the moisture and lipid percentage are summed together to obtain the edible part of a fish.

5.5.2 Fish tissue concentration for radionuclides

The presence of radium in produced water is variable throughout the world. Table 5.5 presents available data for radionuclides in produced water from different platforms. The concentration factor (ratio of concentration in an organ or organism to the concentration in the media) for radionuclides in fish varies depending on type of fish and organ such as flesh, skin or bone (Meinhold and Hamilton, 1992). A study on marine species shows the concentration factors of ^{226}Ra and ^{228}Ra for bone are higher than those for the muscle in Sole, Ray, Sardine, Mackerel, Oil fish, Oyster (*Ostrea sp.*), Clam (*Meretrix sp.*), Green mussel (*Perna viridis*) and Snail (*Petalla radiate*) (Iyengar 1984; Iyengar et el. 1980; Neff, 2002). The concentration factors for fish in soft tissues were in the range of 21-130 (Iyengar et el. 1980). The IAEA (1982) recommended a concentration factor of 100 for the whole fish and this is more representative than the value of IAEA (1985), which suggests a value of 500 for the concentration factor (Hamilton et al. 1992, Iyengar et el. 1980). However, organ based concentration factors vary significantly in fish. Studies on three species of fish suggested that radium is accumulated in bones mostly and least in the flesh (Meinhold and Hamilton, 1992). Concentration factors based on radium content of the whole organism can overestimate the level of radium in the edible portion (Iyengar, 1984). More than 40% of radium in a fish is accumulated in bones and only 6% in the edible flesh (Neff, 2002). Several species of lake fish bioaccumulate radium to higher concentrations in bone than in muscle (Neff, 2002).

Table 5.5 Concentration of radium components in produced water

Platform Information	^{226}Ra (pCi/l)	^{228}Ra (pCi/l)	^{210}Pb (pCi/l)	Source
South Marsh Island 236A, Gulf of Mexico	91±0.13	239±67	12.3±0.53	Hart et al (1996)
Vermilion 214 A, Gulf of Mexico	300±157	229±29	5.6±5.5	Hart et al 1996)
South Marsh Island 130B, Gulf of Mexico	162±43	164±146	7.7±4.7	Hart et al (1996)
High Island 595 CF; Gulf of Mexico	1494±1989	356±19	12.5±2.6	Hart et al (1996)
Eugene Island 189; Louisiana	225	111	--------	Hart et al (1996)
BPT treated Produced Water	172.18	228.4	64.28	Wiedeman et al.(1996)
Ship Shoal 169; Louisiana	260	240	----------	Hart et al (1996)
Open Bay, Louisiana	191.4 (122.4)	250 (163.6)		Meinhold et al. (1996)
Lirette Tank Battery #1, Louisiana	477±30	----------	----------	Mulino et al. (1992)
Golden Meadow Tank Battery #3, Louisiana	143±6.5	149±5.6	----------	Mulino et al. (1992)
South Timbalier Block 52 Platform C, Louisiana	190±7	198±13	----------	Mulino et al. (1992)
Pargo, Brazil (Sampling Period-September 1997)	162	221.4	--------	Vegueria et al. 2002
Pargo, Brazil (Sampling Period-March -1998)	67.5	116.1	--------	Vegueria et al. 2002
Pampo, Brazil (Sampling Period-March -1998)	54	19.71	--------	Vegueria et al. 2002
Pargo, Brazil (Sampling Period-June -1998)	105.3	102.6	---------	Vegueria et al. 2002
Pampo, Brazil (Sampling Period-June -1998)	22.14	62.1	----------	Vegueria et al. 2002
Pampo, Brazil (Sampling Period-August -1998)	51.3	62.1	---------	Vegueria et al. 2002
Gulf of Mexico (42 Platforms)	4-584; Mean 262±156	18-586; Mean 277±146	--------	Stephenson (1992)
EPA 3 Facility Study	4-218 Mean 68±65	4-68 Mean 29±19	----	Stephenson (1992)
Louisiana DEQ Study	0-930 Mean 68±144	0-928 Mean 165±150		Stephenson (1992)
West Cameron 448 (Ambient)	0.30±0.17	0.3	0.37±0.15	Hart et al (1996)
South Marsh Island 186/195 (Ambient reference site)	0.13±0.006	0.6±0.53	0.03±0.06	Hart et al (1996)
Galveston 90 (Ambient reference site)	0.07±0.06	0.7±0.66	0.23±0.21	Hart et al (1996)
Galveston 205 (Ambient reference site)	0.13 ±0.06	0.93±1.21	0.3±0.26	Hart et al (1996)

* Values within bracket () indicate standard deviation; ± Indicates deviation from mean value
BPT= Best Practicable (Available) Technology

The average concentration of ^{226}Ra in shell is 9.3 times higher than that of the soft tissues in mussels (Neff, 2002). Iyengar (1984) determined the average concentration of ^{226}Ra in bone to be 5.0 to 7.9 times higher than that of the soft tissues in fish (*Ophiocephalus sp.*). In lake Trout and Whitefish, this ratio varies between 1.7 and 9.2 and 3.1 to 34.3 respectively (Clulow et al. 1998). The concentration factors for different organs are tabulated in Table 5.6. The data were compiled from Swanson (1983), Iyengar (1984), Iyengar et al. (1980), Hamilton et al. (1992) and Neff (2002).

The concentration factors (*CF*) for radium in flesh follow a lognormal (3.58, 1.29) distribution. In bone/skeleton/shell, the concentration factors also follow a lognormal (5.58,1.1) distribution. The ratios of *CFs* between bone/skeleton and flesh follow a lognormal (2.29,1.20) distribution. The geometric mean of *CFs* between bone/skeleton/shell and flesh was calculated to be 9.9. The edible portion in a fish has a mean value of 78 percent (Table 5.4). The probability plots for the concentration factors are shown in Figures 5.5, 5.6 and 5.7.

The distribution of radium in fish can be calculated from

$$\left.\begin{aligned} & x \times W_t \times C_{flrad} + (1-x) \times W_t \times C_{bonerad} = W_{rad} \\ & \Rightarrow x \times W_t \times C_{flrad} + (1-x) \times W_t \times y \times C_{flrad} = W_{rad} \\ & \Rightarrow C_{flrad} = \frac{W_{rad}}{[x + (1-x)y] \times W_t} \end{aligned}\right\} \quad (5.9)$$

C_{flrad} = Radium concentration in edible part (pCi/kg)

$C_{bonerad}$ = Radium concentration in bone/shell/exoskeleton (pCi/kg)

W_{rad} = Total radium accumulated in fish (pCi)

W_t = Weight of fish (kg)

x = Edible part of a fish

y = Concentration factor ratio of radium in non-edible part to edible part of fish

For mean values of x and y, equation 5.9 can be written as

$$C_{flrad} = \frac{W_{rad}}{2.958 \times W_t} \qquad (5.10)$$

Table 5.6 Organ specific concentration factors of radium in fish

Species (1)	Radium Component (2)	CF (skin) (3)	CF (flesh) (4)	CF (bone, shell, skeleton) (5)	Ratio (5)/(4)	Ratio (5)/(3)
White sucker	Ra	31	12	1793	149.4	57.8
Lake whitefish	Ra	93	3	360	120	3.9
Lake trout	Ra	20	1	10	10	0.5
Oyster	Ra	--	50	500	10	--
Green mussel	Ra	--	46	419	9.1	--
Snail (*Petalla radiate*)	Ra	--	44	256	5.8	--
Sole	^{226}Ra	--	55	370	6.7	--
	^{228}Ra	--	21	160	7.6	--
Oil sardine	^{226}Ra	--	130	610	4.7	--
	^{228}Ra	--	44	180	4.1	--
Ray	^{226}Ra	--	60	65	1.1	--
	^{228}Ra	--	--	98		--
Prawn	^{226}Ra	--	80	360	4.5	--
	^{228}Ra	--	56	300	--	--
Moluscs-marine	^{226}Ra	--	44-63	156-500	2.5-11.4	--
Crustaceans-marine	^{228}Ra	--	35-360	230-800	0.6-22.9	--
Crab	^{228}Ra	--	35	800	22.9	--
Clam	Ra	--	--	200	--	--
Moluscs	Ra	--	2-240	--	--	--

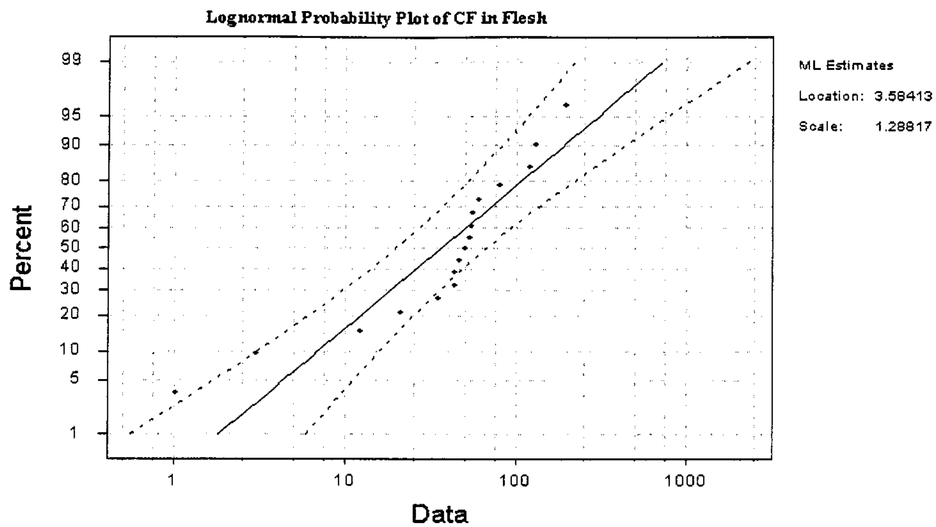


Figure 5.5 Probability plot for concentration factors in flesh/ soft part

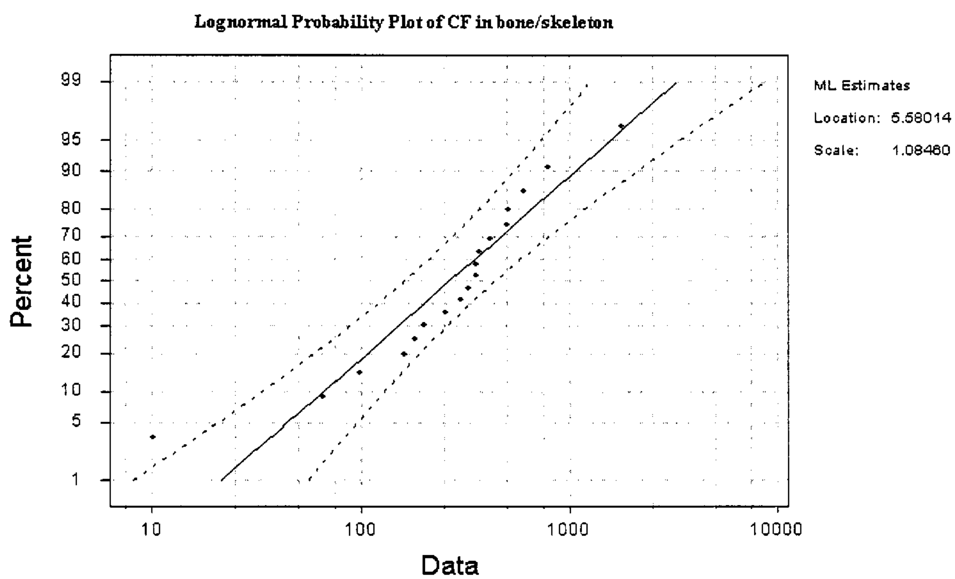


Figure 5.6 Probability plot for concentration factors in bone/skeleton/shell

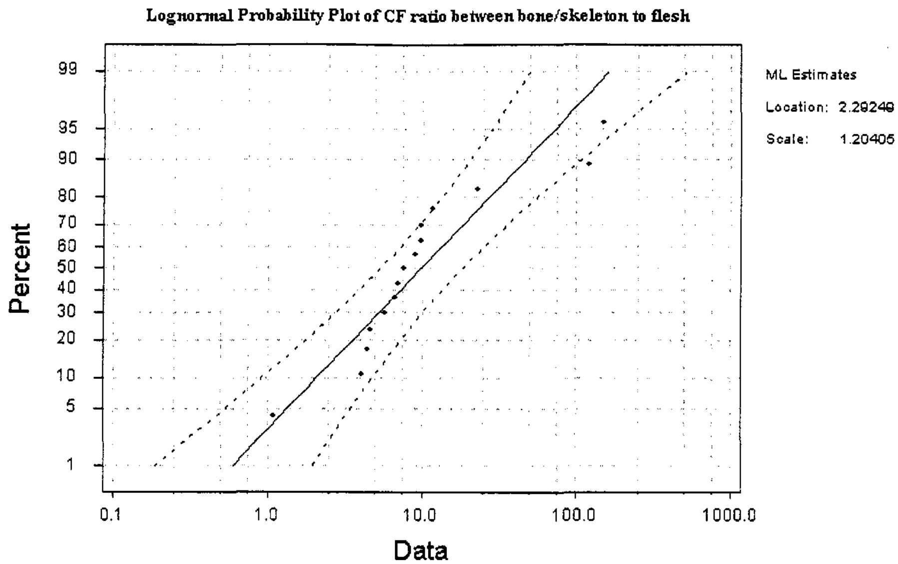


Figure 5.7. Probability plot for concentration factors ratios in bone to soft part

$$W_{rad} = C_{rad} \times W_t \qquad (5.11)$$

$$C_{rad} = C_{\exp} \times BCF \qquad (5.12)$$

where,

C_{exp} is calculated using equation 5.2

BCF = Whole fish bioconcentration

C_{rad} = Radium concentration in whole fish (pCi/kg)

W_t is calculated using equation 3.16 or 3.17 (This equation gives W_t in g. A conversion factor of 1000 is applied to convert W_t from g to kg).

5.6 Exposure quantification for human health risk

The exposure pathway of produced water contaminants through fish ingestion is presented in Figure 5.8. The general procedures involved in exposure assessment are shown in Figure 5.9. From produced water discharges, ingestion of seafood has been assumed as the dominant pathway for uptake of contaminants. Direct contact between humans and contaminants from produced water in the ocean environment has been assumed to be negligible in this study.

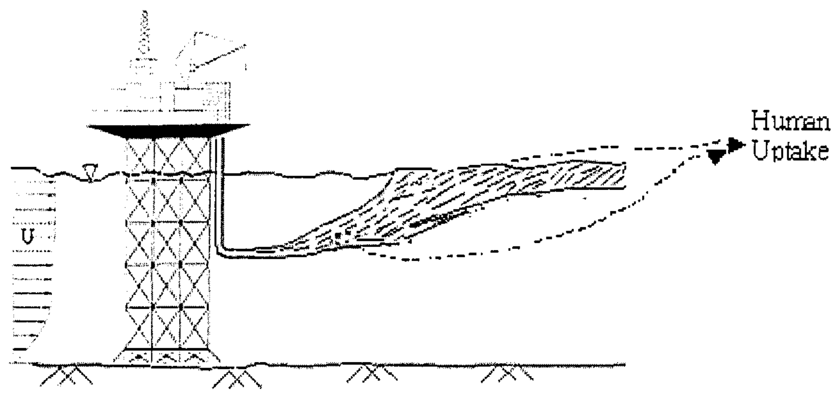


Figure 5.8. Exposure pathway of contaminants through contaminated fish ingestion

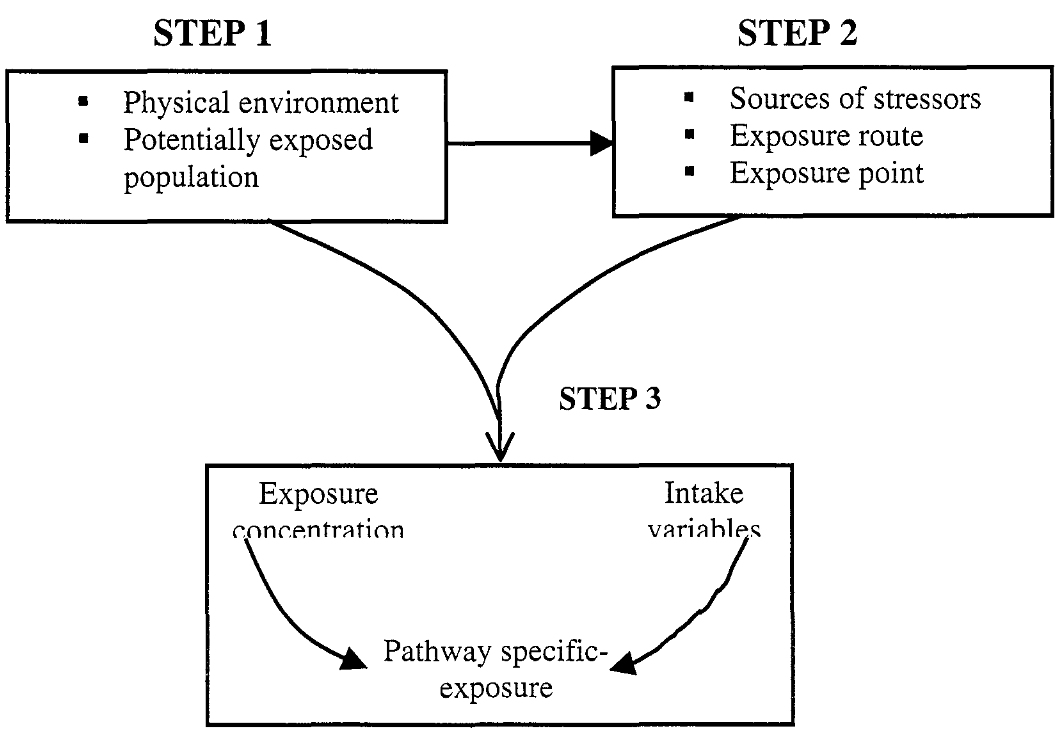


Figure 5.9 Exposure assessment process (modified after USEPA, 1989a)

The intake of contaminants through food ingestion for non-radionuclides was performed by USEPA (1998) as

$$CDI = \frac{C_f \times FIR \times EF \times ED}{BW \times AT} \qquad (5.13)$$

where,

CDI = Chronic daily intake of contaminant (mg/kg-day)

C_f = Concentration in fish tissue (mg/kg of fish)

FIR = Fish ingestion rate (kg/day)

EF = Exposure frequency (days/yr)

ED = Exposure duration (yrs)

BW = Average bodyweight over the exposure period (kg)

AT = Averaging time (days)

Fish ingestion rate (*FIR*)

The USEPA 95th percentile value of fish intake is 132 g/day (USEPA, 1990). Assessment according to age group shows 95th percentile intake of 51 g/day for children below or equal to 14 years and 85 g /day for 15-44 age group (USEPA, 1997). The 99th percentile values are 98 and 138 g/day respectively. Recreational fishermen generally catch fish near the platforms and dilution is less in this region. Hence, recreational fishermen are more susceptible to ingesting produced water contaminated fish than those from the far field (Meinhold et al. 1996). The upper 95th percentile fish ingestion rate of 170 g/day was recommended for Native American Subsistence Populations by USEPA

(1996a). A lognormal distribution to approximate long-term fish ingestion rate was suggested by the USEPA (1996a). The USEPA (1999) used the 99th percentile fish consumption as 177 g/day for human health risk assessment. Meinhold (1996) derived distributions for fish caught near the Open bay platform at Louisiana for the purpose of risk assessment (Table 5.7). This follows a lognormal (3.455, 0.622) distribution where the parameters 3.455 and 0.622 represent the natural log of the median and the standard deviation respectively.

Table 5.7 Fish ingestion rate (Meinhold et al. 1996)

	Intake (g/day)	
	Recreational Fishermen and Families	Children
Arithmetic Mean	38.4	16.6
Median	31.5	13.6
Standard Deviation	26.4	11.6
Minimum	3.3	1.3
Maximum	228.6	115.7
95th Percentile	89.5	38.5

Fraction of fish contaminated with produced water (*FR*)

Throughout the exposure period, it is unrealistic to assume that all the fish ingested are from the contaminated site. A study by the USEPA for the 1-20 age group shows that 0.123 kg/day recreational fish was consumed out of total 0.219 kg/day ingestion. An average meal of 60g/day finfish and shellfish in which 16 g is freshwater finfish, 13g saltwater finfish and 31g shellfish was reported (Schultz et al. 1996). A survey of restaurants shows an average of 889 dishes of 1500 total each week in 1992 were served with seafood. On the basis of data provided by the USEPA (1997), Dellenbarger et al.

(1993) and Schultz et al. (1996), marine fish was almost 50% of the total fish ingestion. Moreover, all the marine fish need not necessarily come from the contaminated zone and therefore, the assumption of 50% of the total ingested fish from the contaminated zone still provides conservative estimates.

Exposure frequency (*EF*)

The USEPA (1989, 1991a) recommended the exposure period for all exposure pathways as 350 days in a year. In this recommendation, a minimum of 2 weeks absence from the exposure scenario has been assumed. This will provide a conservative estimation of risk.

Exposure duration (*ED*)

Exposure duration (*ED*) is the length of time for which exposure to certain stressors occurs through a specific pathway. In the case of some chemicals, indirect exposure may occur even if the source has ceased. Therefore, the USEPA Office of Solid Waste (*OSW*) recommends the use of a default reasonable maximum exposure (*RME*). The number of years that a person is likely to spend in the vicinity of the source can be derived from data on mobility rate and median time in a residence (USEPA, 1998). The USEPA OSW recommended the exposure duration values that are presented in Table 5.8.

Table 5.8 Exposure duration (USEPA, 1998)

Exposure Duration Values	
Recommended Exposure Scenario Receptor	Value (Years)
Child Resident	6
Adult Resident	30
Subsistence Fisher	30
Subsistence Fisher Child	6
Subsistence Farmer	40
Subsistence Farmer Child	6

Body weight (*BW*)

The USEPA (1990a) defined the bodyweight of an adult receptor as 70 kg and a child (1 to 7 years) receptor as 17 kg. The USEPA OSW recommends the child weight as 15 kg for risk assessment purposes (USEPA, 1994). The USEPA (1999) used 70 kg as bodyweight for human health risk assessment.

Averaging time (*AT*)

The human life expectancy is taken to be 70 years (USEPA, 1999). For non-carcinogens, the averaging time is the same as the exposure duration and for carcinogens, the length of life is to be used (USEPA, 1998; Louvar and Louvar, 1998). The USEPA OSW used an averaging time of 70 years. The average life expectancy in different regions of the world is presented in Table 5.9.

5.7 Methodology for human health risk assessment

Equation 5.13 (USEPA, 1998) assumes 100% consumption of contaminated fish. It is unlikely that the total fish consumed by the population at risk is from a contaminated source. The field surveys by Dellenbarger et al. (1993), Schultz et al. (1996), USEPA (1997) presented the distributions of sources. Fish ingestion rate varies widely from region to region based on peoples' choice and fish availability (Meinhold et al. 1996; USEPA, 1990; USEPA, 1996a; USEPA, 1997).

Table 5.9 Human life expectancy (source: Human Development Reports)

Country	Life Expectancy (Years)
Australia	79
Canada	79.2
France	78.7
Japan	81.3
United Kingdom	77.9
United States	76.9
High human development countries	77.1
Medium human development countries	67
Low human development countries	49.4
World	66.7

As discussed before, the lognormal distribution can be used to approximate the long-term fish ingestion rate (USEPA, 1996a). Equation 5.13 can be modified to incorporate the fraction of the produced water contaminated fish ingested from a marine source as follows.

Non-carcinogens

For non-carcinogenic risk assessment as

$$CDI = \frac{C_f \times FIR \times FR \times EF \times 10^{-6}}{BW \times 365} \qquad (5.14)$$

where,

CDI = Chronic daily intake of contaminant (mg/kg-day)

C_f = Concentration in fish tissue (μg/kg of fish)

FIR =Fish ingestion rate (g/day)

FR = Fraction of fish from contaminated source

EF = Exposure frequency (days/yr)

BW = Average bodyweight over the exposure period (kg)

10^{-6} = Conversion factor for fish tissue concentration and fish ingestion

365 = Conversion of averaging time from year to days

Carcinogens (non-radionuclides)

Equation 5.13 can be modified for carcinogenic risk assessment as

$$CDI_C = \frac{C_f \times FIR \times FR \times EF \times ED \times 10^{-6}}{BW \times AT} \qquad (5.15)$$

where,

CDI_C = Chronic daily intake of carcinogen (mg/kg-day)

C_f = Concentration in fish tissue (μg/kg of fish)

FIR =Fish ingestion rate (g/day)

FR = Fraction of fish from contaminated source

EF = Exposure frequency (days/yr)

ED = Exposure duration (yrs)

BW = Average bodyweight over the exposure period (kg)

AT = Averaging time in days; for high human development countries, the life expectancy = 77.1 yrs = 77.1 yrs ×365 days/yrs = 28141 days (Table 5.9).

Radionuclides

To develop a carcinogenic effect, the radionuclides have to be absorbed into the blood. The fraction that is absorbed by blood from the intestinal tract is known as the gastrointestinal absorption factor *(GI)*. Absorption of 100 percent radionuclides from intestinal tract to blood would provide an overestimation of the risk calculation. The USEPA (1999a) tabulated the *GI* factor for radionuclide components: these have been used in this study.

For radionuclides risk assessment, the intake of radium can be quantified by modifying equation 9.18 from Louvar and Louvar (1998) as

$$I_T = C_{flrad} \times FIR \times EF \times ED \times FR \times GI \times 10^{-3} \qquad (5.16)$$

where,

I_T = Total intake radium intake (pCi)

C_{flrad} = Radium concentration in edible part of fish (pCi/kg)

FIR = Daily fish ingestion rate (g/day)

EF = Exposure frequency (days/yr)

ED = Exposure duration (yrs)

FR = Fraction of contaminated fish ingested

GI = Gastrointestinal absorption factor

10^{-3} = Conversion factor from g to kg

5.7.1 Characterization of human health risk

The final step of risk assessment is the calculation of the upper-bound excess lifetime cancer risks and non-carcinogenic hazards for each pathway. Risks and hazards are combined for each of the contaminants to characterize total risk for certain receptors. The carcinogenic risks are averaged throughout the whole span of life and the non-carcinogenic hazards are averaged throughout the exposure periods for the risk assessment. To characterize the risks and hazards, the approaches are discussed as follows.

Non-carcinogen

Risk assessment models assume a threshold value for non-carcinogens and exposure up to that level which will result in no adverse effect (USEPA, 1989). This is determined as

$$HQ = \frac{CDI}{RfD} \qquad (5.17)$$

where,

HQ = Hazard quotient

CDI = Chronic daily intake (Equation 5.6) (mg/kg-day)

R_fD = Reference dose (mg/kg-day)

The value of $HQ \leq 1$ indicates a health-protective level (USEPA, 1989). The total non-carcinogenic hazard attributed through a single exposure pathway is termed as the hazard index *(HI)*. The USEPA (1998) calculated hazard index as

$$HI = \sum_i HQ_i \qquad (5.18)$$

where,

HI = Total hazard for a specific pathway

HQ_i = Hazard quotient for contaminant i

In this approach (USEPA, 1998), all the hazard quotients are assumed to be additive. Assuming the probability of exposure to each contaminant is the same and exposure to each individual contaminant is independent, the hazard index *(HI)* is determined using the probabilistic summation concepts used in equation 5.4.

Carcinogen

For carcinogens, no threshold value is considered. Risk estimates for carcinogens represent the incremental probability that an individual will develop cancer over a lifetime as a result of specific exposure to a carcinogenic chemical (USEPA, 1989). The cancer risk is calculated as

$$CR = CDI_C \times SF \qquad (5.19)$$

where,

CR = Cancer risk

CDI_C = Chronic daily intake of carcinogen (Equation 5.15) (mg/kg-day)

SF = Slope factor (mg/kg-day)$^{-1}$

When the cancer risk is more than 0.01 then the popular one hit model is used for risk estimation. The one hit model is presented by Asante-Duah (1993) as

$$HCR = 1 - e^{(-CDI_C \times SF)} \qquad (5.20)$$

where,

HCR = High cancer risk

USEPA (1998) predicted the total cancer risk as

$$Total\ cancer\ risk = \sum_i CR_i \qquad (5.21)$$

where,

CR_i = Cancer risk from contaminant i

The cancer risk from each contaminant is assumed independent and thus equation 5.4 has been used to determine total cancer risk.

Radionuclide

Radionuclides are carcinogenic and thereby no threshold value is noted. The cancer risk from radionuclides is calculated as

$$CR_{RAD} = I_T \times SF \qquad (5.22)$$

where,

CR_{RAD} = Cancer risk from radionuclides

I_T = Total radium intake (pCi)

SF = Slope factor $(\text{pCi})^{-1}$

The calculation of total radionuclides risk follows equation 5.4

5.7.2 Human health risk assessment framework

The framework for human health risk assessment is presented in Figure 5.10. Sadiq (2001) recommended the combination of ecological risk and total non-carcinogenic and carcinogenic risk to define total environmental risk from drilling waste. For produced water discharges, ecological hazards quotients (*HQ*), human health hazard index (*HI*) and human health cancer risks have been predicted separately. These risks were then compared with the acceptable limits defined by regulatory agencies (e.g. USEPA).

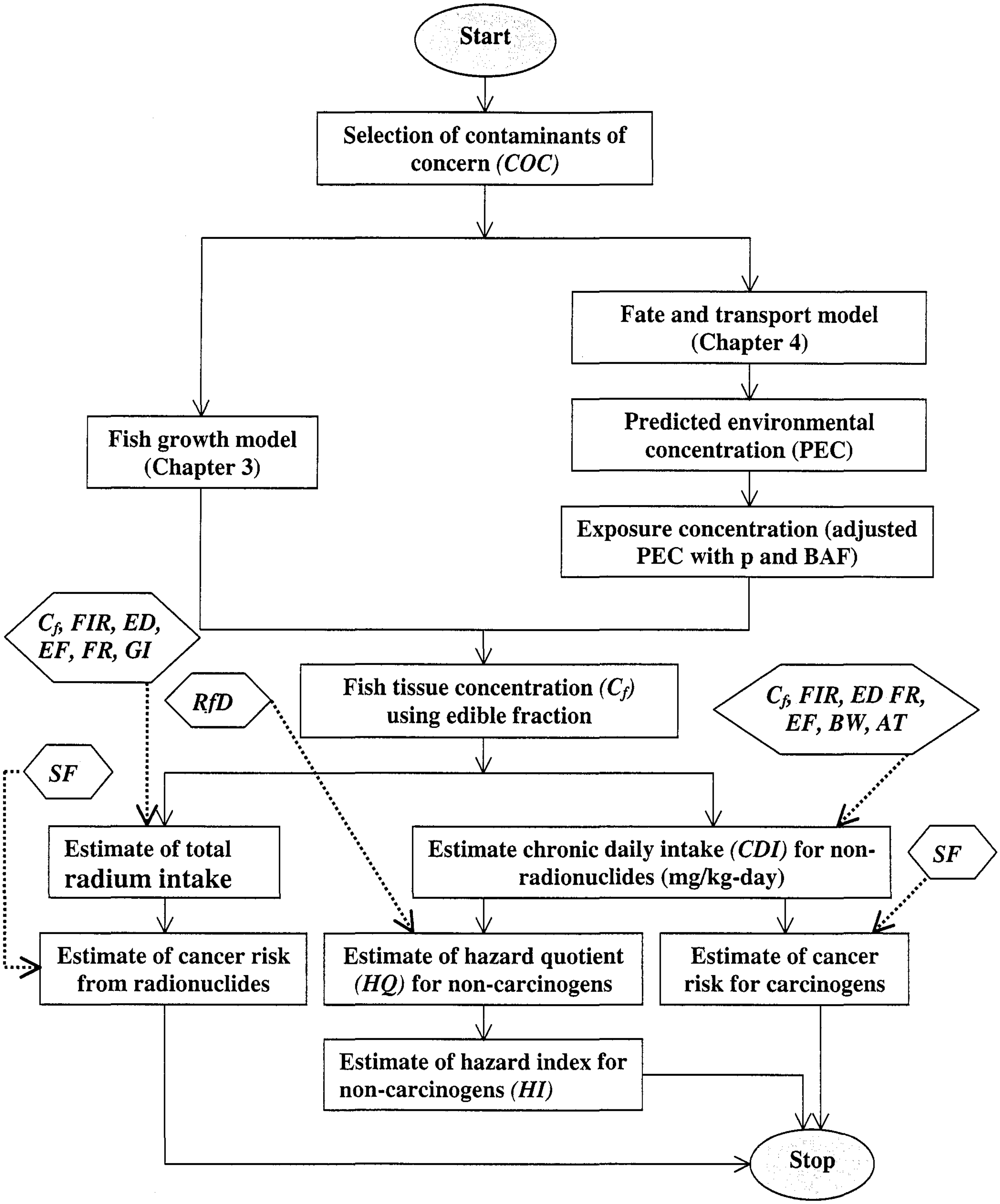


Figure 5.10 Proposed framework for human health risk assessment from produced water

5.8 Summary

The framework for ecological risk assessment based on the US EPA methodology is discussed in this chapter. Selection of endpoints for *ERA* and their relevance are noted. Ecological risk estimation techniques are discussed. The methodology for conversion of predicted environmental concentration (*PEC*) to exposure concentration (*EC*) is illustrated. The average human life expectancy for the developed countries is considered in this study. Modifications of the existing equations to calculate average daily intake (*ADI*) of contaminants have been performed. A new methodology for human health risk assessment is presented in this chapter. In this new methodology, a concept of contaminant distribution between bones/skeleton/shell and edible parts of fish has been introduced. The variability in lipid content and edible parts in fish were incorporated in the new methodology. A separate component to predict human health risk from radionuclides in produced water has been integrated with the new methodology. Radium is accumulated in bones/skeleton/shell of organisms mostly and thus the predicted risk would be lower if the radium in bones/skeleton/shell is avoided. A case study will be performed in chapter 6 using the methodology of this chapter with the models in chapters 3 and 4.

Chapter 6

Risk Characterization: A Hypothetical Case Study

6.1 Introduction

This chapter has been designed to apply the concept and methodology discussed in the previous chapters on a *hypothetical* case study applicable for the oil and gas development activities in the Atlantic Canada. The offshore oil and gas production in Newfoundland has an important role on the Canadian economy by producing around 30% of the total Canadian conventional light crude oil and it contributes approximately 16% of the total gross domestic product (*GDP*) for the province of Newfoundland and Labrador (CNOPB, 2003). As shown in Figure 6.1, most of the oil and gas production activities are on the Grand Banks, which have an area of 93200 km^2, located south-east from Newfoundland at 46°-48° N and 50°-52° W. The Grand Banks is a submarine plateau rising from the continental shelf; has length of 480 km and width of 640 km with a varying water depth ranging from 37 to 183 meters. The location of Grand Banks is presented in Figure 6.1.

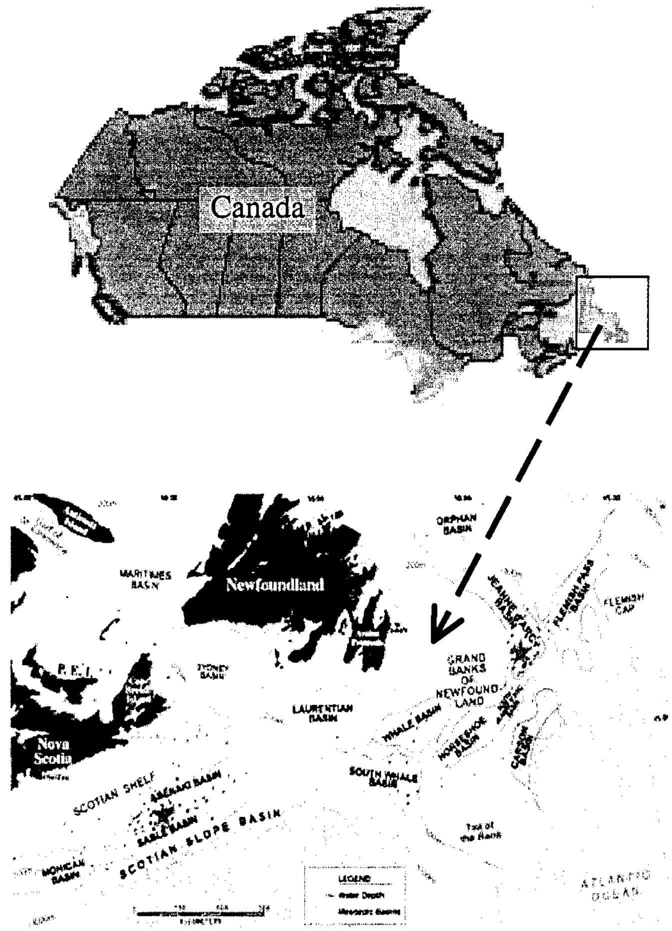


Figure 6.1 Location of Grand Banks; not to scale (source: CNOPB, 2003)

The persistent dense fog, which is formed due to mixing of the cold Labrador Current with the warmer Gulf Stream, is a general characteristic of the Grand Banks. This characteristic along with shallow water depth develops a favorable environment for plankton and fish and therefore the Grand Banks were probably the world's most important international fishing ground until 1977, when Canada extended its offshore jurisdiction to include most of the area. Although the fishing activities have been reduced in the recent years, the economic importance of Grand Banks has been increased as a result of accelerated oil and gas activities. Two oil fields, namely Hibernia and Terra Nova, are already in operation and the White Rose oil field is in development for oil production from 2005. In the year 2002, the average oil production from these two oil fields was estimated as 46805 m^3 (0.3×10^6 bbls) per day with a total production of 16.59 million m^3. The total estimated recoverable oil reserves in the Grand Banks is 335 million m^3, while gas and natural gas liquids (NGLs) are 159 billion m^3 and 52 million m^3 respectively (Table 6.1). As shown in Table 6.1, the three fields on the Grand Banks namely, Hibernia, Terra Nova and White Rose have a cumulative reserve of 74% oil, 77% gas and 83% NGLs (CNOPB, 2003) of the total known reserves on the Grand Banks. The number of wells in a field varies based on the amount of oil and gas extraction. For more extraction, a higher number of producing wells is required (Table 6.1).

Approximately 50000 metric tonnes of pelagic and other finfish were landed in the year 2002 in Newfoundland and Labrador, which contributed 16% of the total catches of pelagic and other finfish in Canada. The fish species available on the Grand Banks are not unique and include both pelagic (Mackerel, Atlantic Herring, Capelin, Tuna etc.), demersal (Atlantic Cod, Haddock, Skate, Halibut, American Plaice etc.) and shellfish (Lobster, Queen/Snow Crab, Sea cucumber etc.). More than 35 fish species, which have economic value, are available on the Grand Banks. Therefore, considering its ecological importance and economic value, the Grand Banks area is an important area to assess ecological risks as a result of exposure to produced water contaminants and human health risks from fish ingestion.

Table 6.1 Oil and gas activities on the Grand Banks (source: CNOPB, 2003)

	Hibernia	Terra Nova	White Rose (Not in operation yet)	Grand Banks
Discovery year	1979	1984	1984	
Location	315 km east southeast of St. John's, NF	350 km east southeast of St. John's, NF and 35 km SE of Hibernia;	350 km east of St. John's, NF and 50 km from both Hibernia and Terra Nova.	
Total number of wells	35(17:oil producers, 12 water injectors and 6 gas injectors	15 (8: oil producers, 5 water injectors and 2 gas injectors	Not started	
Recoverable oil reserve (million m^3)	137.6	64.4	45	334.7
Recoverable gas reserve (billion m^3)	37.2	7.6	76.7	158.6
Natural gas liquids (NGLs) reserve (billion m^3)	25.5	2.2	15.3	51.6
First oil production	November 17, 1997	January 20, 2002	Possibly in 2005	
Oil production in 2002 (million m^3)	10.47	6.12		
Gas production in 2002 (billion m3)	2.44	0.88		
Water production in 2002 (million m^3)	0.45			
Daily oil production in 2002 (m^3)	28,600	18,205	11,925-17,490 (Design capacity)	
Ambient water depth (m)	80	95		

6.2 Characterization of a hypothetical oil platform on the east coast of Canada

The oil and gas activities in eastern Canada started since 1943 through an offshore well off the Prince Edward Island. Since then offshore oil and gas activities have an increasing trend and a positive impact on the Canadian economy. The east coast, especially the Grand Banks, has become one of the important offshore oil and gas sources in Canada over the last decade. Due to the increased offshore activities on the east coast, the degradation of environmental quality in this region has become a concern, and this has led to numerous studies on oil and gas platforms in relation to ecological and human health risk assessment (Mukhtasor, 2001; Sadiq, 2001, Petro-Canada, 1996).

Mukhtasor (2001) developed an ecological risk assessment methodology. In that study, Mukhtasor (2001) used the whole effluent approach in which the total amount of produced water in seawater was selected to characterize the ecological impact. In the current study, human health risk assessment methodology has been developed to characterize human health risks from produced water contaminants. An individual contaminant's toxicity profile has been incorporated in this study, which was not included by Mukhtasor (2001).

A hypothetical oil field on the Grand Banks is considered for application of the developed models and the methodologies to characterize risks to human health and ecological entities. Relevant information for a potential produced water discharge platform in the offshore was collected (e.g. Petro-Canada, 1996). The *FPSO* (Floating Production Storage and Offloading) platform was designed for a capacity of treating 0.212 m^3/s of produced water. The limited available data for the ambient characteristics of the Grand Banks, was defined on the basis of DFO (1999, 2001), Petro-Canada (1996) and Mukhtasor (2001).

The ambient data for the location is presented as follows.

- Water depth: 95 meters

- Air temperature: +26.8°C to −17.3° C with mean of +5°C.
- Wind speed: 9.72 m/sec (average)
- Water temperature: ranges from -1.7°C to 15.4°C
- Fog: seasonal from May to July
- Ice and icebergs: seasonal from April to June

During winter, the water column is cold and at other times it is a two-layer system in which the top layer is approximately 15 m thick. The top layer becomes most stratified in August and can be considered as the depth of mixing layer. In the comparatively shallow Grand Banks, the mean currents are very weak, and vary in the range of 0.05 to 0.15 m/sec (Petro-Canada, 1996). The current speed on the Grand Banks was analyzed by Mukhtasor (2001) and found to follow a lognormal (-3.29, 0.96) distribution. The height of the tide is mostly limited to 1m on the east coast of Newfoundland. The dilution of produced water discharge is directly related to the square of the depth above the discharge and inversely related to the discharge rate (Equations 4.12 and 4.13). The depth of produced water discharge is a variable factor that depends on the ambient water characteristics and the regulation criteria. It has been discussed in section 4.2.2. The depth of the discharge port for this study was assumed as 11m and 8m from the water surface for analyzing two scenarios. The density of produced water varies in the range of 988 kg/m^3 (Bass Strait) to 1185 kg/m^3 (North Sea) while the ambient seawater density varies in the ranges of 1017 kg/m^3 (Gulf of Mexico) to 1027 kg/m^3 (North Sea) as noted in Table 2.3. The information on produced water density for the Grand Banks is not available. The maximum density gradient has been found to be 0.037 and the minimum to be 0.013 for the limited data on positive buoyant produced water.

To characterize the risks, three different density gradients, 0.013, 0.025 and 0.037, were considered for this study. The data on produced water contaminants for the Grand Banks offshore oil and gas platforms are not available yet. The contaminants' type and concentrations in produced water vary significantly from platform to platform and therefore the assumption for the contaminants concentrations needs to be carefully investigated for this case study. Numerous studies on the effects of produced water were conducted in the Gulf of Mexico, Alaska, North Sea, Bass Straits and Java Sea region. Tibbetts et al. (1992) compiled the data for physical properties and metals in produced water for the North Sea, Murchison and Hutton oil fields. Neff et al. (1997) and Neff (2002) studied the worldwide variability of organic chemicals, metals and *NORM* components while OGP (2002) investigated the aromatic compounds in the produced water from 18 platforms in the Norwegian Sector. The details of contaminants' types and concentrations have been discussed in chapter 2. The data in the Table 2.4 have been considered for the case study purpose.

6.3 Prediction of exposure concentration (*EC*) for marine species

The fate and transport models developed by Mukhtasor (2001) have been selected to assess initial dilution and consequently the concentrations in the marine environment (*PEC*). The initial dilution has been predicted using equations 4.12 and 4.13 for deterministic and probabilistic analyses. The related outputs of the models are calculated using equations 4.14 to 4.34. The spatial distributions of the contaminants' concentrations were predicted using the subsequent dispersion models (Equations 4.35-4.41). The contour plots for the concentration distributions were performed using equations 4.42 and 4.43. Upon predicting the environmental concentrations, the exposure concentrations were predicted by incorporating exposure probability (*p*) and the bioavailable fraction (*BAF*). The exposure concentrations are calculated using both deterministic and probabilistic approaches, which have been incorporated with the software.

6.4 Ecological risk assessment

The exposure concentrations (*EC*) for the marine entities are predicted using equation 5.2. The approaches described in Figures 5.2a and 5.2b have been adopted to characterize the ecological risks for the case study. For Figure 5.2a, the mean exposure concentration has been used in predicting hazard quotient (*HQ*) in equation 5.3 while in Figure 5.2b, the uncertainty around the mean exposure concentration has been incorporated through Monte Carlo (*MC*) simulation. If the hazard quotient (HQ) ≤ 1, then the risks induced to the respective organism can be considered as negligible (USEPA, 1998a). The total hazard attributed through a single exposure pathway is called the hazard index *(HI)* and the *HI* has been predicted using the probabilistic summation approach in equation 5.4. Fish, invertebrates (molluscs, crustaceans etc.), micro invertebrates, algae, phytoplankton and zooplankton were suggested as endpoints by the ANWQG (2000) for ecological risk assessment purposes from exposure to organic and inorganic chemicals including metals in marine water column and sediments. In Australia, ecological risk assessment studies have been conducted for a large variety of marine species, which include Sea urchin, Gastropod, Oyster, Scallop, Green Algae, Mussel, Copepod, Amphipod and Prawn (ANWQG, 2000). Sadiq (2001), Neff and Sauer (1996), USEPA online *ECOTOX* and *IRIS* Database, Booman and Foyn (1996), Hamilton et al. (1992), Reish et al. (1976-1980) considered similar species for ecological risk assessment purposes. The advantages of using these indicators are explained by ANWQG (2000). The spatial and temporal distributions of the endpoints are very high and need to be understood. The growth dynamics and the movements of the migratory species for site-specific assessments deserve a high level of understanding to perform ecological risk assessment.

The most abundant contaminants in produced water include Benzene, Toluene, Phenol, Ethylbenzene, Naphthalene, Barium, Cadmium and Chromium. The concentration of *NORM* components in the Gulf of Mexico is the highest of any other known offshore location and thus maximum risk from *NORM* components is expected from this region (Neff, 2002). A selection of five contaminants namely Cadmium, Zinc, Benzene, Toluene and Phenol and their concentrations from Table 2.4 has been considered for this case study. The selection was made on the basis of toxicity and quantity discharged with produced water. The concentrations of *NORM* components from Table 2.4 have also been considered for the risk assessment study.

The total hazards using the deterministic approach for the average and maximum concentrations for the five chemicals considering continuous exposure and exposure probability have been shown in Figure 6.2. The higher the density gradient, the less the effects on fish noticed in Figure 6.2. In this Figure, total hazard is decreasing with the increase of discharge depth. The typical outputs for a density gradient of 0.037, discharge depth 11m and average concentrations in Table 2.4 are shown in Table 6.2. Table 6.3 shows the similar outputs for a discharge depth of 8m and average concentrations in Table 2.4 with the same density gradient.

Table 6.2 Typical outputs of ecological effects (Discharge depth = 11m, Density gradient=0.037, Average concentration)

Name of contaminant	Exposure concentration to fish (μg/l)		*NOEC* (μg/l)	Hazard Quotient to Fish (*HQ*)		Total Hazard	
	Deterministic	Probabilistic		Deterministic	Probabilistic	Deterministic	Probabilistic
Cadmium	9.8E-03	2.8E-03	2.57	3.8E-03	1.1E-03	5.1E-03	1.4E-03
Zinc	2.2E-03	6.2E-04	120	1.8E-05	5.2E-06		
Benzene	4.4E+00	1.25E+00	10200	4.3E-04	1.2E-04		
Toluene	3.5E+00	1.0E+00	5440	6.5E-04	1.8E-04		
Phenol	3.5E+00	9.9E-01	20200	1.7E-04	4.9E-05		

Table 6.3 Typical outputs of ecological effects (Discharge depth = 8m, Density gradient=0.037, Average concentration)

Name of contaminant	Exposure concentration to fish (μg/l)		*NOEC* (μg/l)	Hazard Quotient to Fish (*HQ*)		Total Hazard	
	Deterministic	Probabilistic		Deterministic	Probabilistic	Deterministic	Probabilistic
Cadmium	1.7E-02	4.8E-03	2.57	6.5E-03	1.9E-03	8.7E-03	2.5E-03
Zinc	3.8E-03	1.1E-03	120	3.0E-05	8.8E-06		
Benzene	7.6E+00	2.1E+00	10200	7.4E-04	2.1E-04		
Toluene	6.1E+00	1.7E+00	5440	1.1E-03	3.2E-04		
Phenol	6.0E+00	1.7E+00	20200	3.0E-04	8.4E-05		

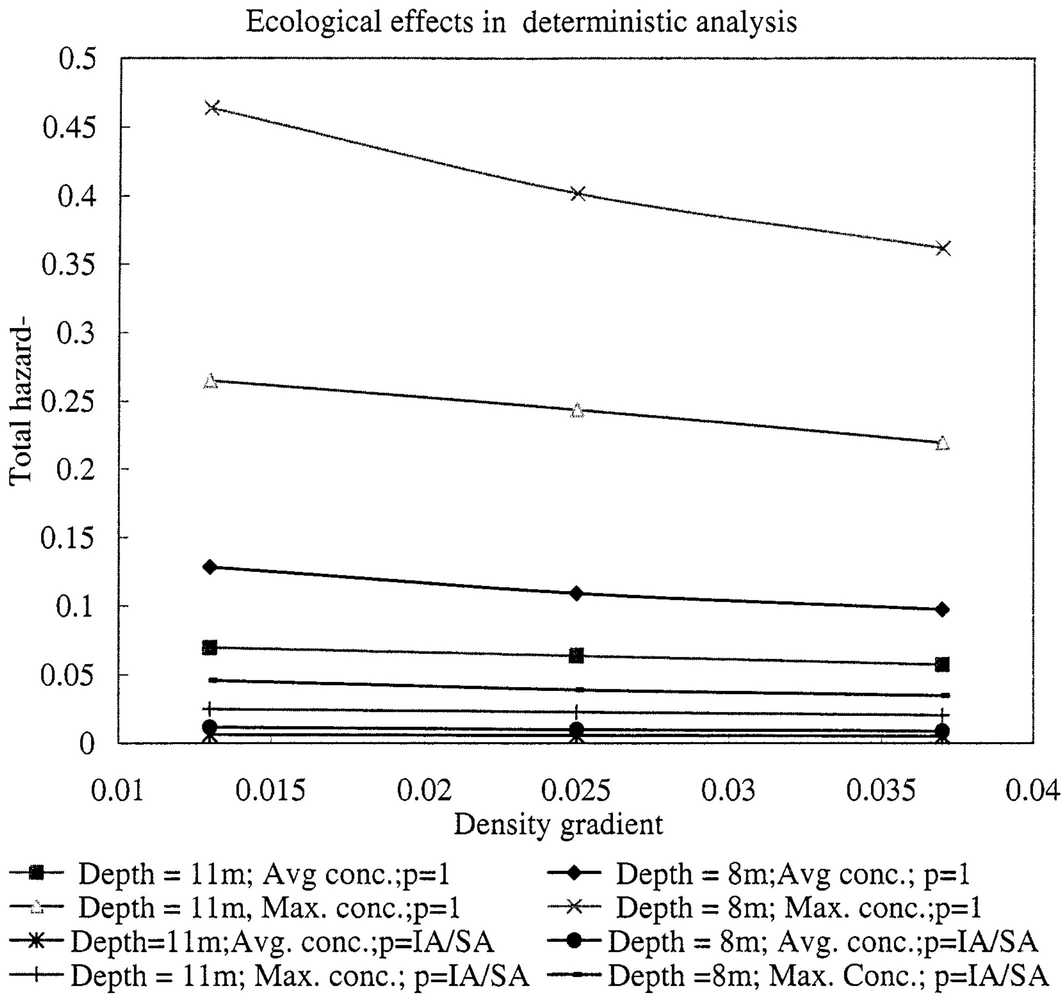


Figure 6.2 Variation of hazard with density gradient in deterministic analysis (IA = impact area; SA = study area; p = exposure probability; p=1 for continuous exposure)

A probabilistic analysis for hazard quotients and total hazard has been conducted. The variations of hazards with density gradient considering continuous exposure and exposure probability have been plotted in Figure 6.3. The predicted hazard is much less than the critical value of 1 in all cases. The hazards considering the exposure probability were predicted to be lower than the hazards predicted using continuous exposure (Figures 6.2 to 6.3). In the deterministic analyses, the highest hazard was predicted to be 0.46

assuming continuous exposure of fish to the produced water plume for a discharge depth of 8 m with the maximum concentrations in Table 2.4, while the value was 0.27 for a discharge depth of 11 m (Figure 6.2). In the probabilistic analyses considering continuous exposure, the highest hazards were predicted as 0.24 and 0.14 respectively for similar conditions (Figure 6.3). Considering the exposure probability (*p*), the highest hazard has been predicted as 0.05 for a discharge depth of 8 m in the deterministic analysis and 0.02 in the probabilistic analysis (Figures 6.2 and 6.3). Tables 6.2 and 6.3 show the differences in individual hazard quotients (*HQ*) and total hazard based on the analyses (deterministic and probabilistic) and discharge depths. For a density gradient of 0.037, the deterministic analysis predicts total hazard as 5.1E-03 while the probabilistic analysis predicts as 1.4E-03 for a discharge depth of 11m (Table 6.2). In case of 8m-discharge depth, the hazard quotients are 8.7E-03 and 2.5E-03 in deterministic and probabilistic analyses respectively (Table 6.3).

For average concentration of cadmium, typical distributions in the marine environment for different discharge depths have been plotted in Figures 6.4 to 6.7. The directions of currents have a significant impact on the distributions of contaminants. The impact area decreases with the increase of discharge depth (Figures 6.4 and 6.5). The impact area increases with the decrease of density gradient (Figures 6.4 and 6.6). The minimum density gradient and lowest depth of discharge is the worst-case scenario in this study (Figure 6.7). The hazard quotients for all the contaminants were less than 1 and thus no or little impact on fish in the marine environment is expected from the produced water contaminants. The total hazards are less than one for all the cases.

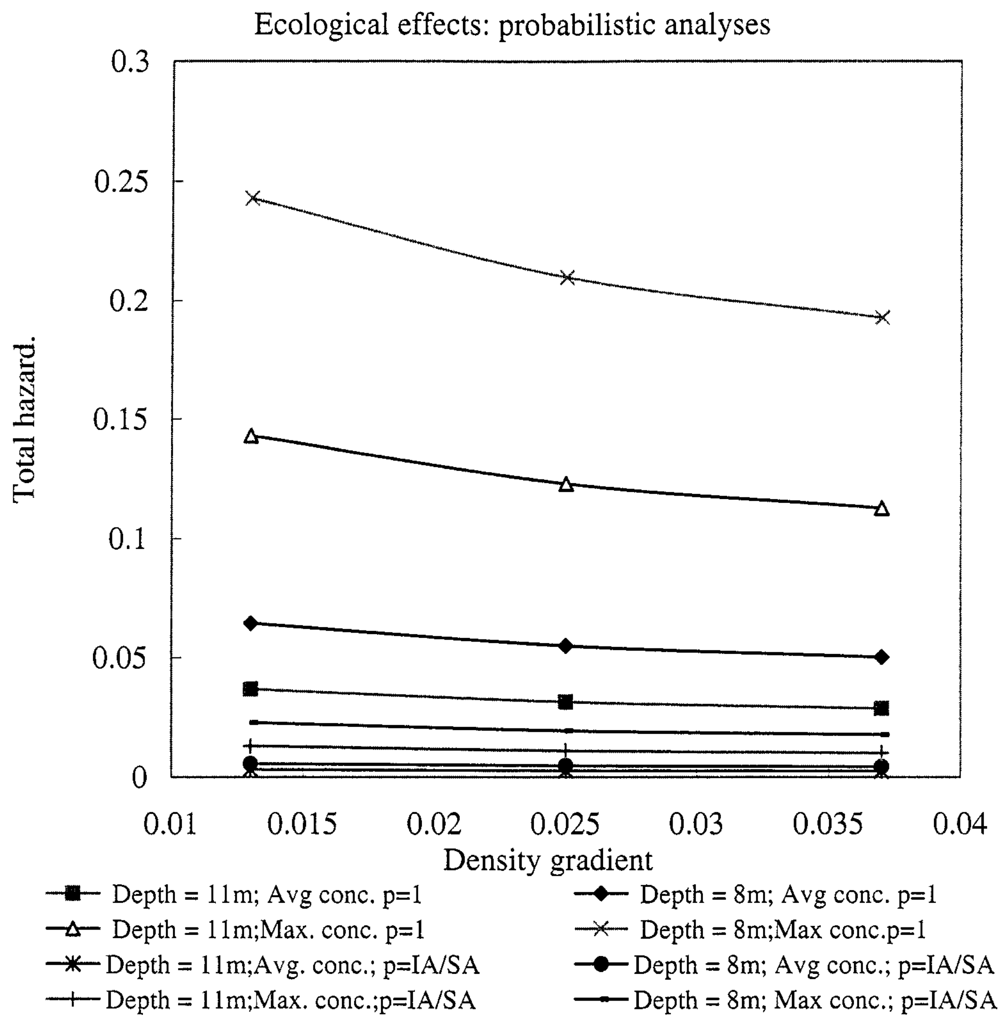


Figure 6.3 Variation of hazard with density gradient in probabilistic analysis (IA = impact area; SA = study area; p= exposure probability; p=1 for continuous exposure)

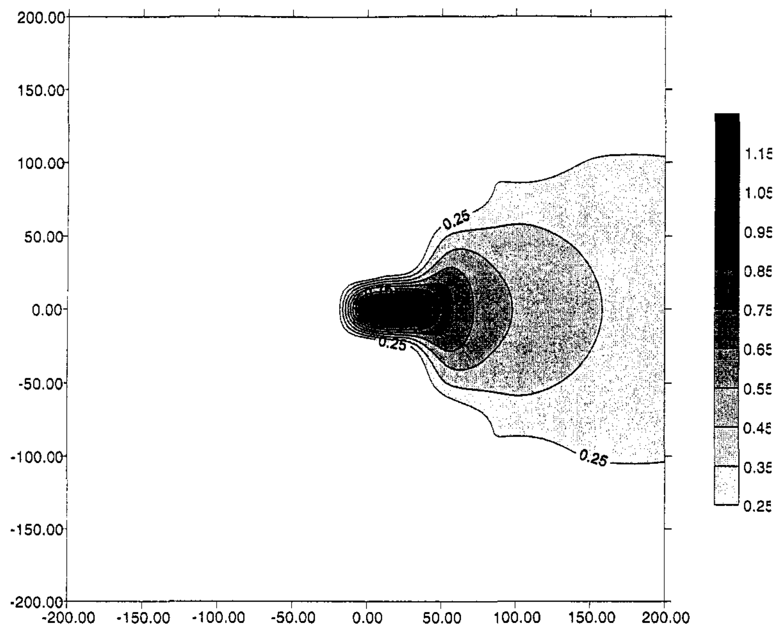


Figure 6.4 Typical concentration distribution (Cadmium at discharge depth = 11m and density gradient = 0.037.

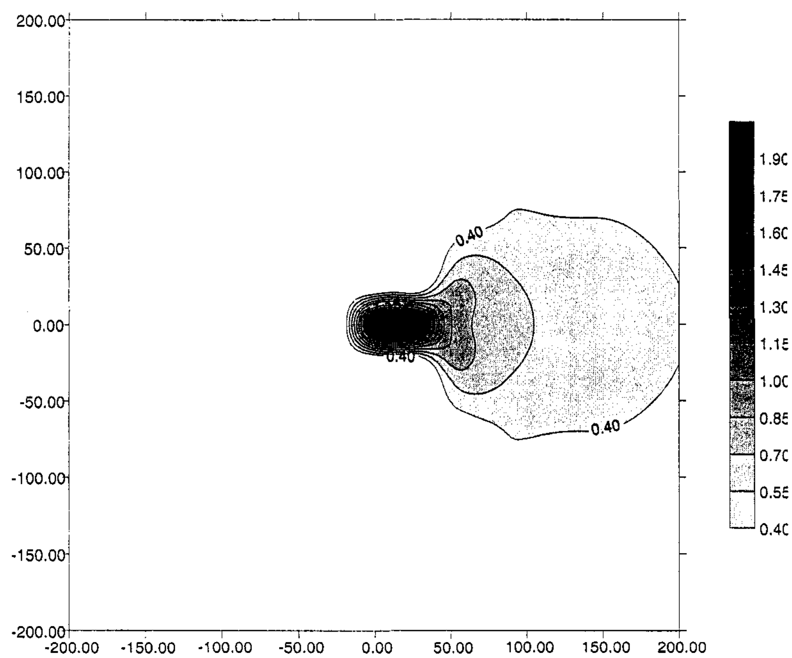


Figure 6.5 Typical concentration distribution (Cadmium at discharge depth = 8m and density gradient = 0.037.

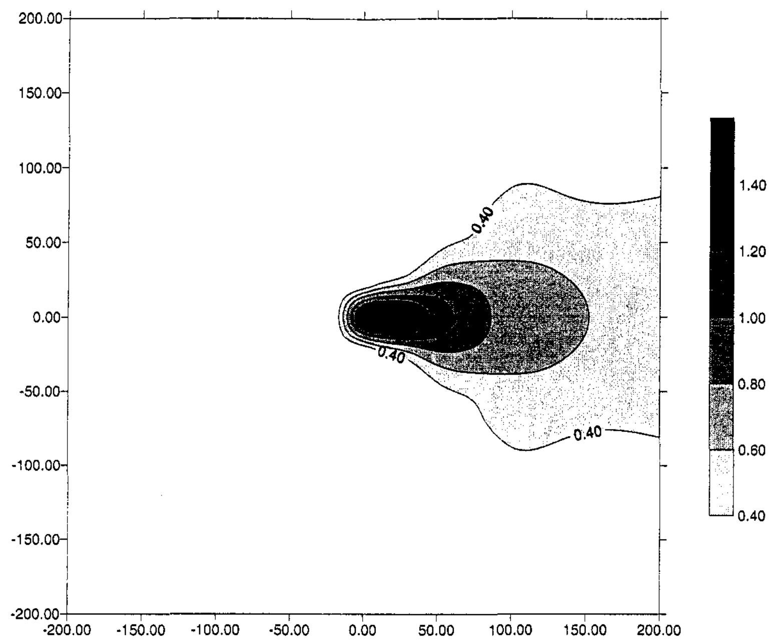


Figure 6.6 Typical concentration distribution (Cadmium at discharge depth = 11m and density gradient = 0.013.

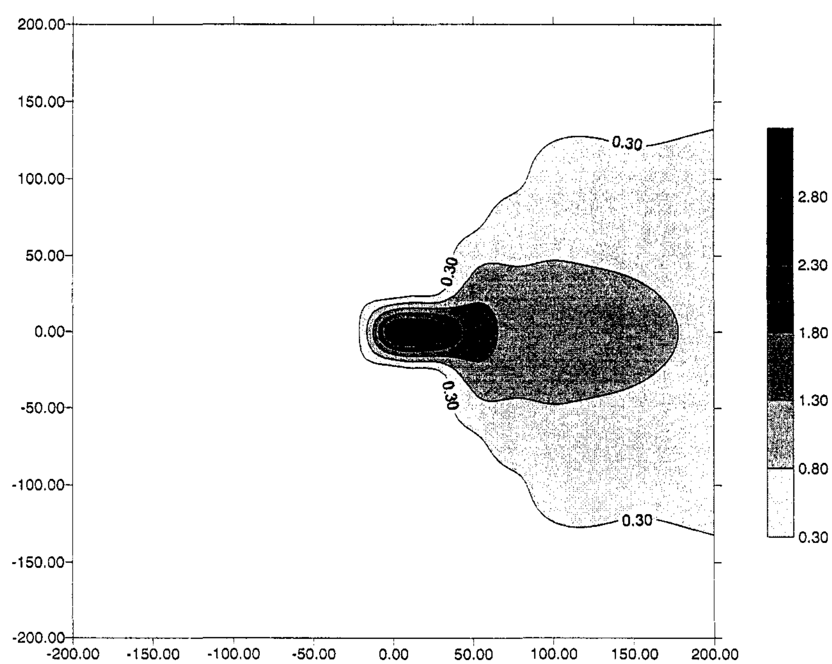


Figure 6.7 Typical concentration distribution (Cadmium at discharge depth = 8m and density gradient = 0.013

6.5 Human health risk assessment

The methodologies described in sections 5.4 to 5.7 have been used to characterize the human health risks from produced water contaminants. The equations 5.4 and 5.6 to 5.22 have been used in characterizing the human health risk. The equations cover the hazard index *(HI)* from non-carcinogens, cancer risk from carcinogens and radionuclides. The probabilistic concept as described in equation 5.4 has been incorporated in the case of exposure to more than one chemical. The carcinogenicity of any contaminant has been denoted by '0' for a non-carcinogen and '1' for a carcinogen. The related parameters to predict hazard quotient (*HQ*), hazard index (*HI*), and cancer risks (*CR*) from different types of contaminants have been discussed in chapter 5.

6.5.1 Hazard assessment

The maximum dose of a chemical that does not pose harmful effects to humans is termed the Reference Dose (*RfD*). The hazard assessment is performed on those chemicals that are non-carcinogens or having both carcinogenic and non-carcinogenic effects to human. Equation 5.14 has been considered to calculate the chronic daily intake (*CDI*) of a chemical. Equation 5.17 predicts individual hazard quotients (*HQ*) for the contaminants. The probabilistic summation approach as noted in equation 5.4 has been incorporated to calculate the hazard index (*HI*) for the concerned contaminants. To calculate the chronic daily intake of contaminants using equation 5.14, the 99^{th} percentile fish consumption rate of 177 g/day has been considered. The USEPA (1999) used a similar fish ingestion rate for human health risk assessment. The hazard index (*HI*) was found to be less than 1 in all the iterations.

6.5.2 Assessment of cancer risk from non-radionuclides

The chemicals in produced water, which have the capacity to develop cancer in the human body, are categorized as carcinogens. Carcinogens do not have any threshold limit. The chronic daily intake (*CDI)* of the carcinogens, which is averaged throughout the expected life period, is multiplied with the slope factors (*SF*) to predict cancer risk. The chronic daily intake was calculated using equation 5.15. The cancer risk from individual contaminant was predicted using equation 5.19 or 5.20 as discussed in the previous chapter. The probabilistic summation approach as equation 5.4 has been used to predict the cumulative cancer risk. Table 6.4 shows toxicological information of the selected contaminants. Only benzene has both carcinogenic and non-carcinogenic effects to human health and the others are non-carcinogenic (Table 6.4).

Table 6.4 Selected contaminants' toxicological data

Name of contaminant	Carcinogenicity	Slope factor *(SF)* $(1/\text{mg/kg-day})^{-1}$	R_fD (mg/kg-day)
Cadmium	No	-	5E-04
Zinc	No	-	2E-01
Benzene	Yes	1.5E-02	4E-03
Toluene	No	-	2E-01
Phenol	No	-	3E-01

The human health hazard quotient for each contaminant has been predicted for four different scenarios. These are shown in Figure 6.8. For lowest density gradient and lowest discharge depth, the predicted hazard quotient was highest (Case I). For higher density gradient, the same depth of discharge results in lower effects to humans (Case II). If the density gradient is the same, the higher the depth of discharge, the lower the effect. (Case I and III, and Case II and IV).

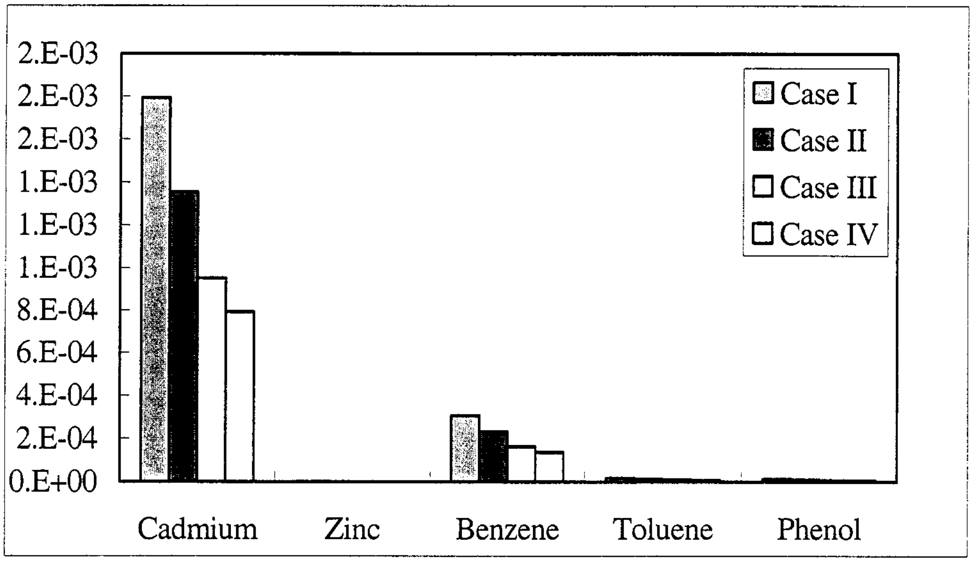


Figure 6.8 Human health hazard quotients in different scenarios

Case I: Discharge depth 8 m and density gradient 0.013
Case II: Discharge depth 8 m and density gradient 0.037
Case III: Discharge depth 11 m and density gradient 0.013
Case IV: Discharge depth 11 m and density gradient 0.037

The hazard index (*HI*) and cancer risk in different scenarios are shown in Table 6.5. For Case I, the hazard index and cancer risk are highest, while in case IV, these are lowest. In all cases, the hazard index and cancer risks are less than the permissible limits.

Table 6.5 Hazard index and cancer risks in different scenarios

	Case I	Case II	Case III	Case IV
Hazard Index (HI)	2.13E-03	1.6E-03	1.1E-03	9.4E-04
Cancer Risk	7.2E-09	5.4E-09	3.8E-09	3.2E-09

Case I: Discharge depth 8 m and density gradient 0.013
Case II: Discharge depth 8 m and density gradient 0.037
Case III: Discharge depth 11 m and density gradient 0.013
Case IV: Discharge depth 11 m and density gradient 0.037

6.5.2 Assessment of cancer risk from radionuclides

The concentrations of radium in fish tissues have been predicted using equations 5.9 to 5.12. The intake of radium by humans through fish ingestion is calculated using equation 5.16 and the cancer risks have been predicted using equation 5.22. The cancer risks for mean concentrations of *NORM* components (Table 2.4) in different discharge scenarios are shown in Figure 6.9. The respective exceedence probabilities are shown in Figure 6.10. The exceedence probability of cancer risk level 1.0E-05 is close to zero in all cases (Figure 6.10). For Case I, the exceedence probability of risk level 1.0E-06 is 28% while for Case IV the exceedence probability is 9.5%.

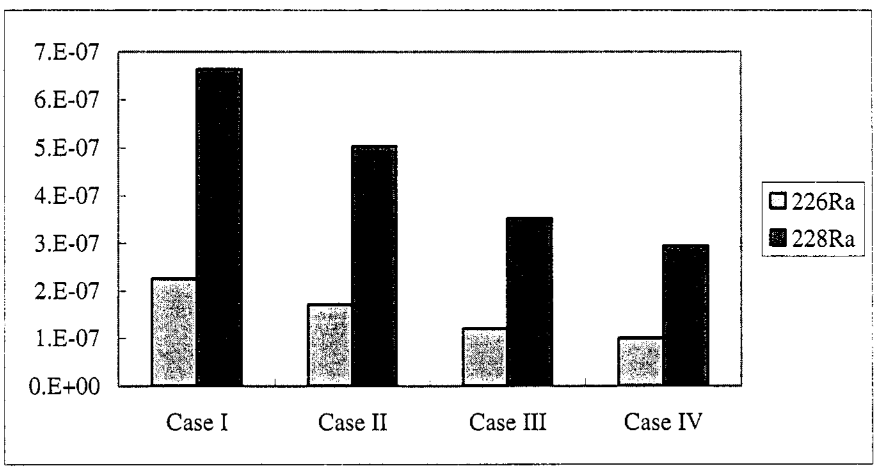


Figure 6.9 Human health cancer risks of NORM components in different scenarios

Case I: Discharge depth 8 m and density gradient 0.013
Case II: Discharge depth 8 m and density gradient 0.037
Case III: Discharge depth 11 m and density gradient 0.013
Case IV: Discharge depth 11 m and density gradient 0.037

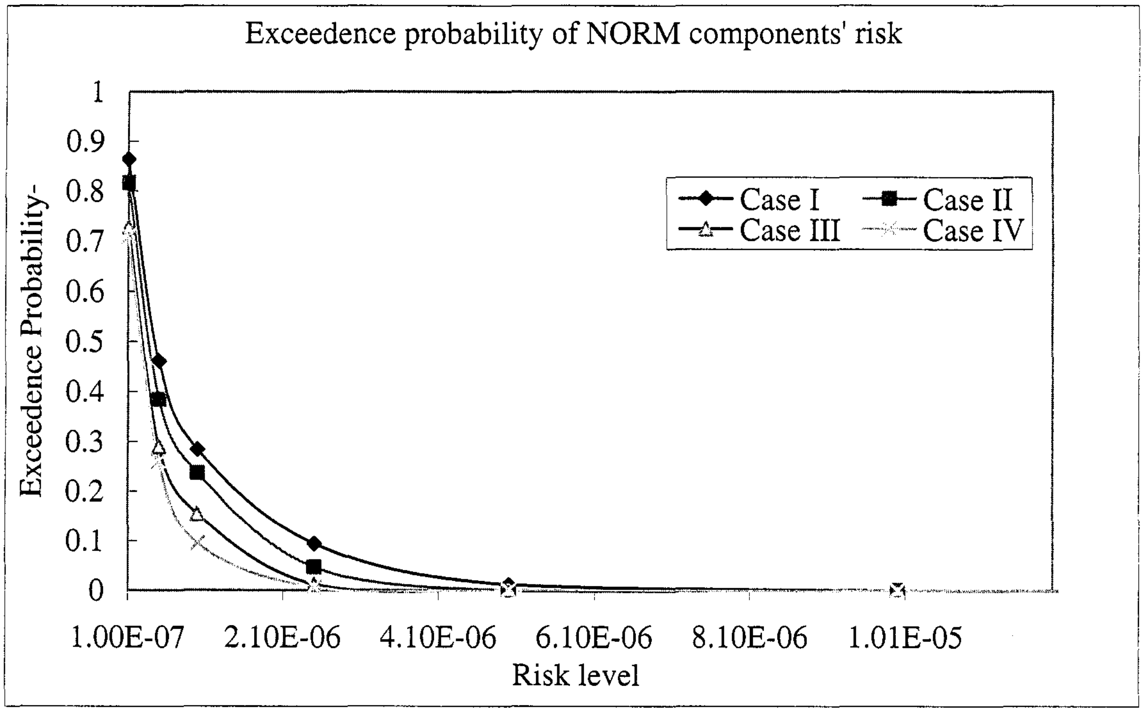


Figure 6.10 Exceedence probability of cancer risks of NORM components in different scenarios

Case I: Discharge depth 8 m and density gradient 0.013
Case II: Discharge depth 8 m and density gradient 0.037
Case III: Discharge depth 11 m and density gradient 0.013
Case IV: Discharge depth 11 m and density gradient 0.037

In another analysis assuming similar field conditions, the new methodology predicts lower cancer risk than the conventional approach (Figure 6.11). In the conventional approach considering the whole body of fish as being edible, the exceedence probability of cancer risk level 1.0E-06 is 48% while this approach predicts this as 22% (Figure 6.11). The mean human health cancer risk in the conventional approach is 2.3E-06 while this approach predicts a value of 8.8E-07, which is 2.6 times lower than the conventional approach.

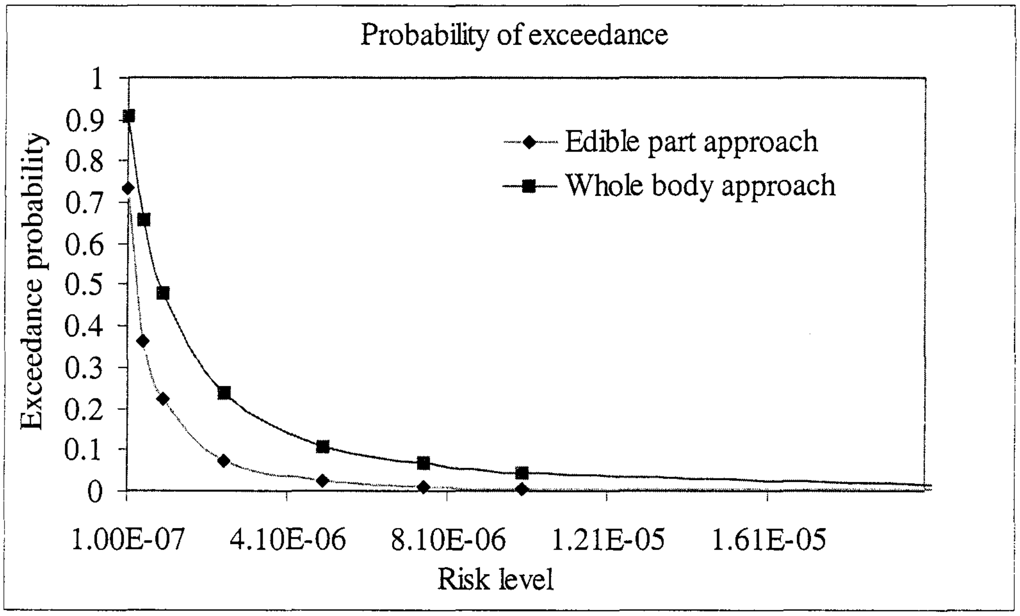


Figure 6.11 Comparison of exceedence probability of cancer risks from NORM components in different approaches

6.6 Summary

A case study considering a *hypothetical* offshore oil field in eastern Canada has been performed in this chapter. The Grand Banks has both economic and ecological importance considering the oil and gas production and the available marine species. Deterministic and probabilistic analyses have been carried out for ecological and human health risk assessment. Two different discharge depths and three density gradients have been considered to evaluate 'what if' scenarios. The higher the depth of discharge, the lower the effects predicted in this study. The density gradients were found to be inversely related to the effects of contaminants. In the probabilistic analyses, the predicted hazard quotients, hazard index and cancer risks are lower than those of the deterministic analyses. For lower discharge depth and lower density gradient, the affected area in the water column is higher (Figures 6.4 to 6.7). The developed human health risk assessment methodologies using the edible parts concept has been applied in this chapter. Figure 6.11 shows the differences in exceedence probability between the conventional approach and this approach of human health risk calculation. This approach results in the lower risk from *NORM* components than the conventional approach. Uncertainty was dealt with by Monte Carlo (*MC*) simulation, which is the most widely used method to consider uncertainty in analysis.

Chapter 7

Conclusions and Recommendations

7.1 Conclusions

The conclusions on the software developed based on the present methodologies to characterize human health risk assessment from produced water contaminants has been presented in this section. The conclusions on the methodologies for ecological risk assessment have also been drawn in this section. The research was carried out through integrating several models and databases and consisted of the following components: (1) development of a database for produced water contaminants; (2) integration of contaminants' database with selected initial dilution and subsequent dispersion models; (3) development of probabilistic fish growth modeling; (4) development of human health cancer and non-cancer risk assessment methodologies using probabilistic concepts; and (5) application of the methodologies to a hypothetical case study from an offshore oil producing platform.

Keeping these objectives in perspectives, the following are the conclusions of this study:

1. A database for produced water contaminants was developed in this study. In the past several risk assessment studies on produced water contaminants were carried out, but

the physical and toxicological data of the contaminants were sparse and thus there was a need to organize the data for produced water contaminants. A total number of 118 contaminants, which mostly belong to produced water, treatment chemicals and other added chemicals during the production period and those of environmental concern have been compiled in this database. The information was compiled from different regulatory agencies and literature. The references for each data can be accessed to know more details about the data. The toxicity data of the contaminants to human and marine biota has been stored in a user-friendly database, which can be accessed conveniently. In addition to the contaminants database, another database for twenty-five marine species, which have economic and ecological importance, has been developed in this study. In that database, the *NOEC* and LC_{50} values for the marine species have been compiled from several regulatory agencies and published literature.

2. As the growth of fish is a continuous process, the growth and lipid variability of fish during the exposure period is important to predict a contaminant's concentration in fish tissue. To incorporate the physical changes of fish within the exposure period, a probabilistic fish growth model has been developed in chapter 3. The available fish growth models have related the length with weight and age with the asymptotic length of fish. The developed models (deterministic and probabilistic) have good agreement with two datasets by Johnson (2000) and Falk et al. (1982). The uncertainty in the growth parameters was incorporated using probabilistic concepts.

3. The available dilution and the subsequent dispersion models have been reviewed in chapter 4. The initial dilution models developed by Mukhtasor (2001) have been used in this study. The contaminant database and the fish growth models have been integrated with the dilution and dispersion models. The previous studies for risk assessment used the whole body concentration of a contaminant and thus a portion of the contaminant was assumed to be in the non-edible parts of the fish. Metals and organic chemicals do not accumulate in the bones, skeleton and exoskeleton significantly. These contaminants mainly accumulate in the edible parts of fish and thus the use of edible parts would provide more realistic prediction of risk from metals and organic chemicals. In this study, the contaminant (non-radionuclide) is distributed within the edible parts of fish and thus predicts a higher concentration in the fish tissue. On the other hand, radium mainly accumulates in bones, skeleton and the exoskeleton of fish. The concentration factors for radium in bones are several times higher than in flesh of fish and thus the use of the whole body concentration would predict higher radium concentration in the edible part of fish, which ultimately predicts higher human health cancer risk through fish ingestion. This approach distributes radium between bones/skeleton/exoskeleton/shell and flesh of fish, which is more realistic for risk assessment purposes.

4. The ecological risk from produced water contaminants has been incorporated within the software using USEPA (1998a) methodology. The fish ingestion rate (*FIR*), exposure duration (*ED*), exposure frequency (*EF*), fraction of contaminated fish (*FR*), human body weight (*BW*), averaging time (*AT*), gastrointestinal absorption factor (*GI*)

and other related parameters have been incorporated with the proposed human health risk assessment methodology. The USEPA (1998) used ingestion of 100% contaminated fish from a marine source, which is a too conservative consideration. For human ingestion, two types of uncertainty are involved: (a) all fish need not necessarily be from a marine source and (b) all the marine fish need not necessarily come from the contaminated zone. This approach has assumed a fraction of 50% contaminated fish ingestion, which is still conservative in relation to the uncertainties. The approaches to predict hazard quotients (*HQ*), hazard index (*HI*), cancer risk (*CR*) from non-radionuclides and radionuclides for human have been discussed in chapter 5. The predicted cancer risk to human from NORM components in produced water was less in this approach than that of the conventional approach.

5. A hypothetical case study based on an oil field in eastern Canada has been performed in chapter 6. Different density gradients and variable discharge depths have been considered in this study. The higher density gradient between produced water and ambient seawater results in lower risk. The higher the depth of discharge, the lower the risk predicted in this study. The distribution of radium between bones/skeleton/exoskeleton and flesh of fish provides lower risk than that of the whole body approach. Minimum ecological impact was predicted in this study. The predicted human health cancer risk was below the permissible range. The predicted results have been compiled in chapter 6. This case study was to show the risk from a typical produced water discharging platform and thus this research would assist in taking the necessary steps to avoid significant risk. In this case study, the predicted

risks were found to be very low from produced water contaminants. But for a shallow water depth situation, the risk may be more because of less dilution. Again, in case of NORM components, the risk from fish consumption needs to be further investigated. The effects of produced water contaminants depend on the location of the site, contaminants available in the produced water from that site, ambient environmental conditions and other human consumption factors. This scientifically grounded refined methodology for predicting human health risk can be applied to different scenarios to achieve a common conclusion about the risk from produced water.

7.2 Recommendations

In setting future research directions, the following recommendations are made:

1. The database compilation was mainly on the basis of produced water contaminants. Compilation of other toxic contaminant's data can enhance the performance of the database in the ecological and human health risk assessment studies. The *NOEC* (No observed effect concentration) and LC_{50} (Lethal concentration that kills 50% of the exposed population) data for a marine species is rare due to the limited sources of available data as most of the tests are interested in some effects to the endpoints. An effort to enhance this database might be undertaken to develop a unique source of toxicological information for the human health and ecological risk assessment studies.

2. The parameters of the available dilution models were not validated. The model was developed for outfalls, which have less density than the ambient water. The density of produced water can be higher than the ambient water as discussed in

chapter 2. The dilution models did not incorporate the effects of tides, waves and effect of stratification in the marine environment. Future research therefore may be carried out in that direction to enhance the performance of the models and parameters validation.

3. The growth model for fish (Trout) has been developed based on the available data from Johnson (2000) and Falk et al. (1982). The probabilistic growth model has incorporated natural variability in predicting the parameters. An effort to validate the growth models for other fish species should be undertaken.

4. The methodologies developed to characterize human health risks from produced water contaminants have integrated the dilution and dispersion models, fish growth models and concentration distribution between edible parts and non-edible parts of fish. The reaction kinetics of the contaminants was not taken into consideration in this approach. Future research to focus on the reaction kinetics using these methodologies should be carried out for more realistic prediction of human health risk.

5. The surrounding sediment ecology, in addition to the marine species, may be affected from produced water contaminants. If the water is shallow enough, the toxic contaminants tend to settle or partition to the sediment. For a shallow water site, this fact needs to be incorporated to predict ecological risk.

7.3 Statement of originality

The originality of this research can be viewed from the following perspectives:

The researcher has been using the toxicological data of different contaminants in produced water to characterize human health and ecological risk. A database for the produced water contaminants has been developed in this research.

To characterize risks from produced water contaminants, a software has been developed in this research. This software system is able to predict ecological hazards and human health risk from produced water contaminants through integrating available models and methodologies with the database in the depository information system. The fish growth models have been developed to characterize physical changes of fish within the exposure periods. The uncertainty in the parameters was dealt with by Monte Carlo (*MC*) simulation. The exposure probability of fish to produced water (p) and the bioavailability of the contaminants as used by USEPA (2000) have been considered in this study. In characterizing human health risk and risk to ecology from a mixture of contaminants, a probabilistic summation approach has been incorporated.

A new concept of contaminants concentration in fish tissue using edible parts of fish has been introduced in this research. This research develops a new framework for human health risk assessment studies in relation to produced water contaminants.

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Appendix 1: Produced Water Contaminants' Database (sample).

NAME	**1,2_DICHLOROETHANE**
CAS_REG_NO	**107-06-2**
MOLECULAR_WEIGHT	**98.96**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	8524	1	TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)	98.97	14	LEACHING_FACTOR	1	
LOG(Kow)	1.48	17	CONVERSION_FACTOR	1	
BIOCONCENTRATION	8	15			
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	10489.84	16	CONC_IN_PW(ug/l)		
HALF_LIFE_(H)	240	18	SED-PORE WAT- P- COEFF		
LOG(Koc)			LC50(ug/l)	230000	134
SS_WATER_PART_COEFF			SF (mg/kg/day)^-1	0.091	10
UF			NOAEL (ug/l)		
NOEC (ug/l)	130000	134	CARCINOGENICITY	1	10
RfD (mg/kg/day)	0				

NAME	**1,2_DICHLOROETHYLENE(CIS)**
CAS_REG_NO	**156-59-2**
MOLECULAR_WEIGHT	**96.94**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	3500	3	TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)	341.38	19	LEACHING_FACTOR	1	
LOG(Kow)	1.86	20	CONVERSION_FACTOR	1	
BIOCONCENTRATION	15	2			
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	26657.8	3	CONC_IN_PW(ug/l)		
HALF_LIFE_(H)	3	21	SED-PORE WAT- P- COEFF		
LOG(Koc)			LC50(ug/l)		
SS_WATER_PART_COEFF			SF (mg/kg/day)^-1		
UF	3000	6	NOAEL (ug/l)		
NOEC (ug/l)			CARCINOGENICITY	1	6
RfD (mg/kg/day)	0.01	6			

NAME	**1,2_DICHLOROETHYLENE(TRANS)**
CAS_REG_NO	**156-60-5**
MOLECULAR_WEIGHT	**96.94**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	6300	3	TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)	680.74	16	LEACHING_FACTOR	1	
LOG(Kow)	2.06	20	CONVERSION_FACTOR	1	
BIOCONCENTRATION	22	19			
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	45318.3	3	CONC_IN_PW(ug/l)		
HALF_LIFE_(H)			SED-PORE WAT- P- COEFF		
LOG(Koc)	1.77	12	LC50(ug/l)	220000	137
SS_WATER_PART_COEFF			SF (mg/kg/day)^-1		

UF	1000	10	NOAEL (ug/l)	0.1	10
NOEC (ug/l)			CARCINOGENICITY	0	10
RfD (mg/kg/day)	0.02	10			

NAME **2- HEXANONE (METHYLBUTYL KETONE)**

CAS_REG_NO **591-78-6**

MOLECULAR_WEIGHT **100.16**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	17500	28	TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)	9.1575	28	LEACHING_FACTOR	1	
LOG(Kow)	1.38	28	CONVERSION_FACTOR	1	
BIOCONCENTRATION	1.1994	28			
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	1600	28	CONC_IN_PW(ug/l)	35.8	118
HALF_LIFE_(H)	170	28	SED-PORE WAT- P- COEFF	0.94	28
LOG(Koc)	0.993	28	LC50(ug/l)	428000	138
SS_WATER_PART_COEFF	2.9506	28	SF (mg/kg/day)^-1		
UF			NOAEL (ug/l)		
NOEC (ug/l)			CARCINOGENICITY		
RfD (mg/kg/day)					

NAME **2-4_DIMETHYLPHENOL**

CAS_REG_NO **105-67-9**

MOLECULAR_WEIGHT **122.17**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	6200	22	TOXICITY_WEIGHING_FACTOR	0.0024	24
HLC(Pa m^3/mol)	0.638	22	LEACHING_FACTOR	1	
LOG(Kow)	2.3	20	CONVERSION_FACTOR	1	
BIOCONCENTRATION	151.356	23			
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	13.06	22	CONC_IN_PW(ug/l)	117	118
HALF_LIFE_(H)	77	27	SED-PORE WAT- P- COEFF		
LOG(Koc)	2.19	25	LC50(ug/l)	40000	136
SS_WATER_PART_COEFF	194.94	28	SF (mg/kg/day)^-1		
UF	3000	10	NOAEL (ug/l)	50	26
NOEC (ug/l)	30000	136	CARCINOGENICITY	0	10
RfD (mg/kg/day)	0.02	10			

NAME **2-BUTANONE (METHYLETHYL-KETONE)**

CAS_REG_NO **78-93-3**

MOLECULAR_WEIGHT **72.11**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	240000	28	TOXICITY_WEIGHING_FACTOR	0.0001	128
HLC(Pa m^3/mol)	3.6355	28	LEACHING_FACTOR	1	
LOG(Kow)	0.29	28	CONVERSION_FACTOR	1	
BIOCONCENTRATION	0.0975	28			
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	12100	28	CONC_IN_PW(ug/l)	122	118
HALF_LIFE_(H)	55	28	SED-PORE WAT- P- COEFF	0.0767	28
LOG(Koc)	-0.0973	28	LC50(ug/l)	400000	134
SS_WATER_PART_COEFF	0.2398	28	SF (mg/kg/day)^-1		0

UF	1000	10	NOAEL (ug/l)	1771	26
NOEC (ug/l)	400000	134	CARCINOGENICITY	0	10
RfD (mg/kg/day)	0.05	10			

NAME **2-METHYLNAPTHALENE**

CAS_REG_NO **91-57-6**

MOLECULAR_WEIGHT **142.19**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	24.6	99	TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)	40.52	100	LEACHING_FACTOR	1	
LOG(Kow)	3.86	99	CONVERSION_FACTOR	1	
BIOCONCENTRATION	190	99			
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	7.33	99	CONC_IN_PW(ug/l)	67.2	118
HALF_LIFE_(H)	9840	27	SED-PORE WAT- P- COEFF		
LOG(Koc)	3.474	99	LC50(ug/l)	1300	139
SS_WATER_PART_COEFF			SF (mg/kg/day)^-1		
UF			NOAEL (ug/l)		
NOEC (ug/l)			CARCINOGENICITY		
RfD (mg/kg/day)					

NAME **ACENAPHTHENE**

CAS_REG_NO **83-32-9**

MOLECULAR_WEIGHT **154.21**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	3.8	28	TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)	12.174	28	LEACHING_FACTOR	1	
LOG(Kow)	3.92	28	CONVERSION_FACTOR	1	
BIOCONCENTRATION	415.55	28			
			AMBIENT CONC (ug/l)		124
VAPOUR_PRESSURE(Pa)	0.3	28	CONC_IN_PW(ug/l)	0.001	119
HALF_LIFE_(H)	550	28	SED-PORE WAT- P- COEFF	327.38	28
LOG(Koc)	3.533	28	LC50(ug/l)	3100	140
SS_WATER_PART_COEFF	1023.07	28	SF (mg/kg/day)^-1		
UF	3000	10	NOAEL (ug/l)	175	26
NOEC (ug/l)	1000	134	CARCINOGENICITY	0	10
RfD (mg/kg/day)	0.06	10			

NAME **ACETIC ACID**

CAS_REG_NO **64-19-7**

MOLECULAR_WEIGHT **60.05**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	6841000	28	TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)	0.0182	28	LEACHING_FACTOR	1	
LOG(Kow)	-0.31	28	CONVERSION_FACTOR	1	
BIOCONCENTRATION	0.0245	28			
			AMBIENT CONC (ug/l)		125
VAPOUR_PRESSURE(Pa)	2079	28	CONC_IN_PW(ug/l)	132	120
HALF_LIFE_(H)	55	28	SED-PORE WAT- P- COEFF	0.0193	28
LOG(Koc)	-0.697	28	LC50(ug/l)	180000	170

SS_WATER_PART_COEFF	0.0602	28	SF (mg/kg/day)^-1		
UF			NOAEL (ug/l)		
NOEC (ug/l)			CARCINOGENICITY		
RfD (mg/kg/day)					

NAME **ACETONE (2- PROPANONE)**

CAS_REG_NO **67-64-1**

MOLECULAR_WEIGHT **58.09**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	452880	28	TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)	3.72	29	LEACHING_FACTOR	1	
LOG(Kow)	-0.24	4	CONVERSION_FACTOR	1	
BIOCONCENTRATION	1	30			
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	30789	31	CONC_IN_PW(ug/l)	913	118
HALF_LIFE_(H)	20	21	SED-PORE WAT- P- COEFF	0.0226	28
LOG(Koc)	-0.627	28	LC50(ug/l)	100000	142
SS_WATER_PART_COEFF	0.0708	28	SF (mg/kg/day)^-1		
UF	1000	10	NOAEL (ug/l)	100	26
NOEC (ug/l)	403000	143	CARCINOGENICITY	0	10
RfD (mg/kg/day)	0.1	10			

NAME **ALUMINIUM**

CAS_REG_NO **7429-90-5**

MOLECULAR_WEIGHT **30.01**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	59400	99	TOXICITY_WEIGHING_FACTOR	0.064	128
HLC(Pa m^3/mol)		0	LEACHING_FACTOR	1	
LOG(Kow)	0.33	99	CONVERSION_FACTOR	1	
BIOCONCENTRATION	3.2	99			
			AMBIENT CONC (ug/l)	110	129
VAPOUR_PRESSURE(Pa)	1.1649E-07	99	CONC_IN_PW(ug/l)	1072	118
HALF_LIFE_(H)		0	SED-PORE WAT- P- COEFF	1500	99
LOG(Koc)	1.155	99	LC50(ug/l)	310	144
SS_WATER_PART_COEFF		0	SF (mg/kg/day)^-1		0
UF		0	NOAEL (ug/l)		0
NOEC (ug/l)			CARCINOGENICITY	0	0
RfD (mg/kg/day)	1	99			

NAME **ALUMINIUM PHOSPHIDE**

CAS_REG_NO **20859-73-8**

MOLECULAR_WEIGHT **57.96**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	192000	99	TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)			LEACHING_FACTOR	1	
LOG(Kow)	-0.17	99	CONVERSION_FACTOR	1	
BIOCONCENTRATION	3.2	99			
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	4.52E-09	99	CONC_IN_PW(ug/l)		
HALF_LIFE_(H)			SED-PORE WAT- P- COEFF		
LOG(Koc)	1.155	99	LC50(ug/l)	100	145
SS_WATER_PART_COEFF			SF (mg/kg/day)^-1		

UF	100	26	NOAEL (ug/l)	0.043	26
NOEC (ug/l)	0.043		CARCINOGENICITY	0	
RfD (mg/kg/day)	0.0004	26			

NAME **ANTHRACENE**

CAS_REG_NO **120-12-7**

MOLECULAR_WEIGHT **178.24**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	0.045	32	TOXICITY_WEIGHING_FACTOR	0.351	24
HLC(Pa m^3/mol)	3.96	33	LEACHING_FACTOR	1	
LOG(Kow)	4.34	35	CONVERSION_FACTOR	1	
BIOCONCENTRATION	9120	34			
			AMBIENT CONC (ug/l)	0.05	130
VAPOUR_PRESSURE(Pa)	0.001	32	CONC_IN_PW(ug/l)		
HALF_LIFE_(H)	11.36		SED-PORE WAT- P- COEFF		
LOG(Koc)	4.15	12	LC50(ug/l)	13300	146
SS_WATER_PART_COEFF	1023.07	28	SF (mg/kg/day)^-1		
UF	3000	10	NOAEL (ug/l)	1000	26
NOEC (ug/l)			CARCINOGENICITY	0	10
RfD (mg/kg/day)	0.3	10			

NAME **ANTIMONY**

CAS_REG_NO **1440-36-0**

MOLECULAR_WEIGHT **121.8**

		Reference			**Reference**
SOLUBILITY_(g/m^3)			TOXICITY_WEIGHING_FACTOR	0.0125	24
HLC(Pa m^3/mol)			LEACHING_FACTOR	1	
LOG(Kow)			CONVERSION_FACTOR	1	
BIOCONCENTRATION	1475	98			
			AMBIENT CONC (ug/l)	10	129
VAPOUR_PRESSURE(Pa)	0		CONC_IN_PW(ug/l)	166	118
HALF_LIFE_(H)			SED-PORE WAT- P- COEFF	3981.1	97
LOG(Koc)			LC50(ug/l)	7250	134
SS_WATER_PART_COEFF	63095.7	97	SF (mg/kg/day)^-1		
UF	1000	10	NOAEL (ug/l)		
NOEC (ug/l)	6200	134	CARCINOGENICITY	0	
RfD (mg/kg/day)	0.0004	10			

NAME **MANGANESE**

CAS_REG_NO **7439-96-5**

MOLECULAR_WEIGHT **54.938**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	87200	99	TOXICITY_WEIGHING_FACTOR	0.056	24
HLC(Pa m^3/mol)			LEACHING_FACTOR	1	
LOG(Kow)	0.23	99	CONVERSION_FACTOR	1	
BIOCONCENTRATION	3.2	99			
			AMBIENT CONC (ug/l)	0.5	123
VAPOUR_PRESSURE(Pa)	0	99	CONC_IN_PW(ug/l)	1301	118
HALF_LIFE_(H)			SED-PORE WAT- P- COEFF		
LOG(Koc)	1.155	99	LC50(ug/l)	170	164
SS_WATER_PART_COEFF			SF (mg/kg/day)^-1		

UF	1	10	NOAEL (ug/l)	0.14	26
NOEC (ug/l)			CARCINOGENICITY	0	
RfD (mg/kg/day)	0.14	26			

NAME	**NAPTHALENE**
CAS_REG_NO	**91-20-3**
MOLECULAR_WEIGHT	**128.18**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	31	28	TOXICITY_WEIGHING_FACTOR	0.6597	24
HLC(Pa m^3/mol)	43	28	LEACHING_FACTOR	1	
LOG(Kow)	3.37	28	CONVERSION_FACTOR	1	
BIOCONCENTRATION	117.21	28			
			AMBIENT CONC (ug/l)	0.066	124
VAPOUR_PRESSURE(Pa)	10.4	28	CONC_IN_PW(ug/l)	144	118
HALF_LIFE_(H)	170	28	SED-PORE WAT- P- COEFF	92.3	28
LOG(Koc)	2.983	28	LC50(ug/l)	1000	132
SS_WATER_PART_COEFF	288.34	28	SF (mg/kg/day)^-1		
UF	10000	10	NOAEL (ug/l)	71	26
NOEC (ug/l)			CARCINOGENICITY	0	
RfD (mg/kg/day)	0.004	10			

NAME	**N-DOCOSANE**
CAS_REG_NO	**629-97-0**
MOLECULAR_WEIGHT	

		Reference			**Reference**
SOLUBILITY_(g/m^3)			TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)			LEACHING_FACTOR	1	
LOG(Kow)			CONVERSION_FACTOR	1	
BIOCONCENTRATION					
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)			CONC_IN_PW(ug/l)	38	118
HALF_LIFE_(H)			SED-PORE WAT- P- COEFF		
LOG(Koc)			LC50(ug/l)	500000	134
SS_WATER_PART_COEFF			SF (mg/kg/day)^-1		
UF			NOAEL (ug/l)		
NOEC (ug/l)	500000	134	CARCINOGENICITY		
RfD (mg/kg/day)					

NAME	**NICKEL**
CAS_REG_NO	**7440-02-0**
MOLECULAR_WEIGHT	**58.7**

		Reference			**Reference**
SOLUBILITY_(g/m^3)			TOXICITY_WEIGHING_FACTOR	0.6759	24
HLC(Pa m^3/mol)			LEACHING_FACTOR	0.043	37
LOG(Kow)			CONVERSION_FACTOR	0.99	38
BIOCONCENTRATION	100	96			
			AMBIENT CONC (ug/l)	1.05	123
VAPOUR_PRESSURE(Pa)			CONC_IN_PW(ug/l)	109	118
HALF_LIFE_(H)			SED-PORE WAT- P- COEFF	7943.3	97
LOG(Koc)	0		LC50(ug/l)	8000	127
SS_WATER_PART_COEFF	39810.78	78	SF (mg/kg/day)^-1	0.84	77
UF			NOAEL (ug/l)	0	
NOEC (ug/l)			CARCINOGENICITY	1	77
RfD (mg/kg/day)	0				

NAME	**O_CRESOL**
CAS_REG_NO	**95-48-7**
MOLECULAR_WEIGHT	**108.13**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	26000	28	TOXICITY_WEIGHING_FACTOR	0	
HLC(Pa m^3/mol)	0.1702	28	LEACHING_FACTOR	1	
LOG(Kow)	1.98	28	CONVERSION_FACTOR	1	
BIOCONCENTRATION	4.775	28			
			AMBIENT CONC (ug/l)	30000	133
VAPOUR_PRESSURE(Pa)	40	28	CONC_IN_PW(ug/l)	121	118
HALF_LIFE_(H)	17	28	SED-PORE WAT- P- COEFF	3.76	28
LOG(Koc)	1.593	28	LC50(ug/l)	10200	175
SS_WATER_PART_COEFF	11.74	28	SF (mg/kg/day)^-1	0	
UF	1000	6	NOAEL (ug/l)	0	
NOEC (ug/l)	0		CARCINOGENICITY	0	
RfD (mg/kg/day)	0.05	6			

NAME	**O-XYLENE**
CAS_REG_NO	**95-47-6**
MOLECULAR_WEIGHT	**106.2**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	220	28	TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)	564.79	28	LEACHING_FACTOR	1	
LOG(Kow)	3.15	28	CONVERSION_FACTOR	1	
BIOCONCENTRATION	70.6269				
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	1170	28	CONC_IN_PW(ug/l)	86.1	118
HALF_LIFE_(H)	550	28	SED-PORE WAT- P- COEFF	55.59	28
LOG(Koc)	2.763	28	LC50(ug/l)	6000	139
SS_WATER_PART_COEFF	173.742	28	SF (mg/kg/day)^-1		
UF	100	65	NOAEL (ug/l)	0	
NOEC (ug/l)			CARCINOGENICITY	0	
RfD (mg/kg/day)	2	65			

NAME	**P_CRESOL**
CAS_REG_NO	**106-44-5**
MOLECULAR_WEIGHT	**108.13**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	22600	3	TOXICITY_WEIGHING_FACTOR	0.007	128
HLC(Pa m^3/mol)	0.0973	79	LEACHING_FACTOR	1	
LOG(Kow)	1.94	5	CONVERSION_FACTOR	1	
BIOCONCENTRATION	18.2	80			
			AMBIENT CONC (ug/l)	21000	133
VAPOUR_PRESSURE(Pa)	17.32	3	CONC_IN_PW(ug/l)	149	118
HALF_LIFE_(H)	4008	82	SED-PORE WAT- P- COEFF	0	
LOG(Koc)	1.76	81	LC50(ug/l)	14000	176
SS_WATER_PART_COEFF	11.5		SF (mg/kg/day)^-1	0	
UF	1000	6	NOAEL (ug/l)	0	
NOEC (ug/l)	0		CARCINOGENICITY	0	
RfD (mg/kg/day)	0.05	6			

NAME	**PENTACHLOROPHENOL**
CAS_REG_NO	**87-86-5**

MOLECULAR_WEIGHT **266.35**

		Reference			Reference
SOLUBILITY_(g/m^3)	14	28	TOXICITY_WEIGHING_FACTOR	0	
HLC(Pa m^3/mol)	0.28	28	LEACHING_FACTOR	1	
LOG(Kow)	5.12	4	CONVERSION_FACTOR	1	
BIOCONCENTRATION	5610.09	28			
			AMBIENT CONC (ug/l)	0	
VAPOUR_PRESSURE(Pa)	0.00415	28	CONC_IN_PW(ug/l)	0	
HALF_LIFE_(H)	550	28	SED-PORE WAT- P- COEFF	4416.26	28
LOG(Koc)	4.66	28	LC50(ug/l)	4600	135
SS_WATER_PART_COEFF	13800.83	28	SF (mg/kg/day)^-1	0.12	10
UF	100	6	NOAEL (ug/l)	3	26
NOEC (ug/l)	0		CARCINOGENICITY	1	10
RfD (mg/kg/day)	0.03	6			

NAME **PHENANTHRENES**

CAS_REG_NO **85-01-8**

MOLECULAR_WEIGHT **178.24**

		Reference			Reference
SOLUBILITY_(g/m^3)	1.15	99	TOXICITY_WEIGHING_FACTOR		
HLC(Pa m^3/mol)	3.24	28	LEACHING_FACTOR	1	
LOG(Kow)	4.46	99	CONVERSION_FACTOR	1	
BIOCONCENTRATION	1857.68	28			
			AMBIENT CONC (ug/l)	0.017	124
VAPOUR_PRESSURE(Pa)	0.000112	99	CONC_IN_PW(ug/l)	90	120
HALF_LIFE_(H)	550	28	SED-PORE WAT- P- COEFF	1462.36	28
LOG(Koc)	4.32	99	LC50(ug/l)	438	178
SS_WATER_PART_COEFF	4569.88	28	SF (mg/kg/day)^-1		
UF			NOAEL (ug/l)		
NOEC (ug/l)			CARCINOGENICITY		
RfD (mg/kg/day)					

NAME **PHENOL**

CAS_REG_NO **108-95-2**

MOLECULAR_WEIGHT **94.1**

		Reference			Reference
SOLUBILITY_(g/m^3)	88360	28	TOXICITY_WEIGHING_FACTOR	0.0193	24
HLC(Pa m^3/mol)	0.05	28	LEACHING_FACTOR	1	
LOG(Kow)	1.46	28	CONVERSION_FACTOR	1	
BIOCONCENTRATION	27.54	28			
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	47	28	CONC_IN_PW(ug/l)	553	118
HALF_LIFE_(H)	55	28	SED-PORE WAT- P- COEFF	1.135	28
LOG(Koc)	1.07	28	LC50(ug/l)	24800	179
SS_WATER_PART_COEFF	3.547	28	SF (mg/kg/day)^-1		
UF	300	26	NOAEL (ug/l)	0	
NOEC (ug/l)	20200	179	CARCINOGENICITY	0	
RfD (mg/kg/day)	0.3	26			

NAME **SELENIUM**

CAS_REG_NO **7782-49-2**

MOLECULAR_WEIGHT **78.96**

		Reference			Reference

SOLUBILITY_(g/m^3)	81400	99	TOXICITY_WEIGHING_FACTOR	0.0797	24
HLC(Pa m^3/mol)	0		LEACHING_FACTOR	1	37
LOG(Kow)	0.24	99	CONVERSION_FACTOR	0.998	38
BIOCONCENTRATION	50000	36			
			AMBIENT CONC (ug/l)	4	127
VAPOUR_PRESSURE(Pa)	1215000	99	CONC_IN_PW(ug/l)	250	118
HALF_LIFE_(H)	0		SED-PORE WAT- P- COEFF	3981.1	97
LOG(Koc)	1.155	99	LC50(ug/l)	6700	134
SS_WATER_PART_COEFF	25118.8	97	SF (mg/kg/day)^-1	0	
UF	15	10	NOAEL (ug/l)	0.015	26
NOEC (ug/l)	2000	134	CARCINOGENICITY	0	
RfD (mg/kg/day)	0.003	10			

NAME **SILVER**

CAS_REG_NO **744-02-24**

MOLECULAR_WEIGHT **107.9**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	70500	99	TOXICITY_WEIGHING_FACTOR	6.0871	24
HLC(Pa m^3/mol)			LEACHING_FACTOR	1	37
LOG(Kow)	0.23	99	CONVERSION_FACTOR	0.85	38
BIOCONCENTRATION	87.71	98			
			AMBIENT CONC (ug/l)	0.3	126
VAPOUR_PRESSURE(Pa)	0	99	CONC_IN_PW(ug/l)	252	118
HALF_LIFE_(H)			SED-PORE WAT- P- COEFF	3981.1	97
LOG(Koc)	1.155	99	LC50(ug/l)	58000	134
SS_WATER_PART_COEFF	158489.3	97	SF (mg/kg/day)^-1		
UF	2	10	NOAEL (ug/l)	0	
NOEC (ug/l)	6400	134	CARCINOGENICITY	0	
RfD (mg/kg/day)	0.003	10			

NAME **STRONTIUM**

CAS_REG_NO **7440-24-6**

MOLECULAR_WEIGHT **87.62**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	80400	99	TOXICITY_WEIGHING_FACTOR	0	
HLC(Pa m^3/mol)	0		LEACHING_FACTOR	1	
LOG(Kow)	0.23	99	CONVERSION_FACTOR	1	
BIOCONCENTRATION	3.2	99			
			AMBIENT CONC (ug/l)	7700	125
VAPOUR_PRESSURE(Pa)	7.664E-39	99	CONC_IN_PW(ug/l)	205500	118
HALF_LIFE_(H)	0		SED-PORE WAT- P- COEFF	0	
LOG(Koc)	1.155	99	LC50(ug/l)	170	164
SS_WATER_PART_COEFF	0		SF (mg/kg/day)^-1	0	
UF	300	26	NOAEL (ug/l)	190	26
NOEC (ug/l)	190		CARCINOGENICITY	0	
RfD (mg/kg/day)	0.6	26			

NAME **STYRENE**

CAS_REG_NO **100-42-5**

MOLECULAR_WEIGHT **104.16**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	300		TOXICITY_WEIGHING_FACTOR	0.0741	24
HLC(Pa m^3/mol)	284.65	19	LEACHING_FACTOR	1	
LOG(Kow)	3.05	28	CONVERSION_FACTOR	1	
BIOCONCENTRATION	56.1	28			
			AMBIENT CONC (ug/l)		

VAPOUR_PRESSURE(Pa)	880		CONC_IN_PW(ug/l)	0	
HALF_LIFE_(H)	170	28	SED-PORE WAT- P- COEFF	44.16	28
LOG(Koc)	2.663	28	LC50(ug/l)	9100	134
SS_WATER_PART_COEFF	138.008	28	SF (mg/kg/day)^-1	0.0303	10
UF	1000	26	NOAEL (ug/l)	200	26
NOEC (ug/l)	5100	134	CARCINOGENICITY	1	10
RfD (mg/kg/day)	0.2	26			

NAME **TIN**

CAS_REG_NO **7440-31-5**

MOLECULAR_WEIGHT **120.73**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	7909	99	TOXICITY_WEIGHING_FACTOR	0.3011	24
HLC(Pa m^3/mol)			LEACHING_FACTOR	1	
LOG(Kow)	1.29	99	CONVERSION_FACTOR	1	
BIOCONCENTRATION	100	99			
			AMBIENT CONC (ug/l)	3	127
VAPOUR_PRESSURE(Pa)	0	99	CONC_IN_PW(ug/l)	305	118
HALF_LIFE_(H)			SED-PORE WAT- P- COEFF	5011.87	97
LOG(Koc)	1.155	99	LC50(ug/l)	170	164
SS_WATER_PART_COEFF	79432.82	97	SF (mg/kg/day)^-1		
UF	100	62	NOAEL (ug/l)		
NOEC (ug/l)			CARCINOGENICITY		
RfD (mg/kg/day)	0.6	99			

NAME **TOLUENE**

CAS_REG_NO **108-88-3**

MOLECULAR_WEIGHT **92.13**

		Reference			**Reference**
SOLUBILITY_(g/m^3)	515	28	TOXICITY_WEIGHING_FACTOR	0.0018	24
HLC(Pa m^3/mol)	679.79	28	LEACHING_FACTOR	1	
LOG(Kow)	2.69	28	CONVERSION_FACTOR	1	
BIOCONCENTRATION	24.49	28			
			AMBIENT CONC (ug/l)		
VAPOUR_PRESSURE(Pa)	3800	28	CONC_IN_PW(ug/l)	3370	118
HALF_LIFE_(H)	550	28	SED-PORE WAT- P- COEFF	19.3	28
LOG(Koc)	2.3	28	LC50(ug/l)	36200	148
SS_WATER_PART_COEFF	60.243	28	SF (mg/kg/day)^-1		
UF	1000	10	NOAEL (ug/l)	0	
NOEC (ug/l)	5440	148	CARCINOGENICITY	0	
RfD (mg/kg/day)	0.2	10			

Appendix 2: Typical NOEC Database (Columns represent µg/l and Day)

Contaminant's Name	***ARSENIC***					Polychates		
Molluscs	973	28	Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	280-973	
Copepod			Clams			Crustacean larvae		
SeaStar			Algae	48		Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	631	29-51	Pelecypod			Gastropod larvae		
Rotifer			Annelids			Amphipod		

Contaminant's Name	***BORON***					Polychates		
Molluscs			Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	6000(FW)	
Copepod			Clams			Crustacean larvae		
SeaStar			Algae	400-5200	14	Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp			Pelecypod			Gastropod larvae		
Rotifer			Annelids			Amphipod		

Contaminant's Name	***CADMIUM***					Polychates		
Molluscs			Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	122	
Copepod			Clams			Crustacean larvae		
SeaStar			Algae	8.2-32(FW)		Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	4-5	28	Pelecypod			Gastropod larvae		
Rotifer	18 (FW)	2	Annelids			Amphipod		

Contaminant's Name	***CHROMIUM***					Polychates		
Molluscs			Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans		
Copepod			Clams			Crustacean larvae		
SeaStar			Algae	4.8-1000	7	Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	88	29-51	Pelecypod			Gastropod larvae		
Rotifer	2000 (FW)	2	Annelids			Amphipod		

Contaminant's Name			***COPPER***			Polychates		
Molluscs			Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	1.7-42	10-14
Copepod			Clams			Crustacean larvae		
SeaStar			Algae			Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	77	4	Pelecypod			Gastropod larvae		
Rotifer			Annelids			Amphipod		

Contaminant's Name			***LEAD***			Polychates		
Molluscs	880-904	7	Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	25	29-51
Copepod			Clams			Crustacean larvae		
SeaStar			Algae	8-27	14	Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp			Pelecypod			Gastropod larvae		
Rotifer			Annelids	8	183-274	Amphipod		

Contaminant's Name			***MERCURY***			Polychates		
Molluscs	0.12-1014	5	Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	0.8-10	7-11
Copepod			Clams			Crustacean larvae		
SeaStar			Algae	0.9-88		Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms	4	7
Shrimp			Pelecypod			Gastropod larvae		
Rotifer			Annelids	3.4-18	7-28	Amphipod		

Contaminant's Name			***MOLYBDENUM***			Polychates		
Molluscs			Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	670-2200(FW	2-4
Copepod			Clams			Crustacean larvae		
SeaStar			Algae	10000-150		Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp			Pelecypod			Gastropod larvae		
Rotifer			Annelids			Amphipod		

Contaminant's Name			***PHENOL***			Polychates		
Molluscs			Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans		

Copepod			Clams			Crustacean larvae		
SeaStar			Algae	1 mmol/l	2	Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	2410	27	Pelecypod			Gastropod larvae		
Rotifer			Annelids			Amphipod		

Contaminant's Name	*SELENIUM*					Polychates		
Molluscs			Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	85 (FW)	21
Copepod			Clams			Crustacean larvae		
SeaStar			Algae	13000-198	3-6	Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp			Pelecypod			Gastropod larvae		
Rotifer			Annelids			Amphipod		

Contaminant's Name	*SILVER*					Polychates		
Molluscs	5-42	8-28	Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	2.5-42	28-38
Copepod			Clams			Crustacean larvae		
SeaStar			Algae	0.8-3.5	5-14	Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp			Pelecypod			Gastropod larvae		
Rotifer			Annelids	5-28	21-71	Amphipod		

Contaminant's Name	*VANADIUM*					Polychates		
Molluscs	13000	9	Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	7000	9
Copepod			Clams			Crustacean larvae		
SeaStar			Algae	100	13	Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp			Pelecypod			Gastropod larvae		
Rotifer			Annelids	2000	9	Amphipod		

Contaminant's Name	*ZINC*					Polychates		
Molluscs	15-27500	7-11	Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	15-2100	8-28
Copepod			Clams			Crustacean larvae		

SeaStar	Algae			Phytoplankton
Crab	Decapod			Polychateslarvae
Mysid	Mussels			Echinoderms
Shrimp	Pelecypod			Gastropod larvae
Rotifer	Annelids	70-3260	7-9	Amphipod

Appendix 3: Typical LC50 Database (Columns represent ug/l and Day)

Contaminant's Name			***1,1,2 TRICHLOROETHANE***			Polychates	190000	4
Molluscs			Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	43000-8200	2-4
Copepod			Clams			Crustacean larvae		
SeaStar			Algae	60000-26	2-4	Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels	140000	14	Echinoderms		
Shrimp	43000	10	Pelecypod			Gastropod larvae		
Rotifer			Annelids			Amphipod	50000	14

Contaminant's Name			***ARSENIC***			Polychates		
Molluscs	1500-7400		Gastropod			SeaUrchin		
Bivalve	3500	4	Oyster			Crustaceans	1000	8-51
Copepod	907	4	Clams			Crustacean larvae	230	4
SeaStar			Algae	6-9		Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	2319	4	Pelecypod	3490	4	Gastropod larvae		
Rotifer			Annelids	3000-750		Amphipod		

Contaminant's Name			***BENZENE***			Polychates		
Molluscs	165000-92		Gastropod			SeaUrchin		
Bivalve	190000	4	Oyster			Crustaceans	3300-38000	
Copepod	82 ppm	<=4	Clams			Crustacean larvae		
SeaStar			Algae	41000	8	Phytoplankton		
Crab	12840	4	Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	97800	1	Pelecypod			Gastropod larvae		
Rotifer	>1000	1	Annelids			Amphipod		

Contaminant's Name			***CADMIUM***			Polychates	12000	4
Molluscs			Gastropod	3500	4	SeaUrchin		
Bivalve	1600-2500	4	Oyster	20-25	6	Crustaceans	15-100	4
Copepod	1800	4	Clams			Crustacean larvae	250-380	4
SeaStar	7100		4 Algae			Phytoplankton		
Crab	175000	14	Decapod	14000	4	Polychateslarvae	220	4
Mysid	15	4	Mussels	500-1000	1	Echinoderms	7100-10000	4
Shrimp	200-300	4	Pelecypod	1480	4	Gastropod larvae		
Rotifer	5200	3	Annelids			Amphipod	320	5

Contaminant's Name			***CHROMIUM***			Polychates	1440-1890	7
Molluscs			Gastropod	105000	4	SeaUrchin		
Bivalve	57000	4	Oyster	611	4	Crustaceans	3400-45000	4
Copepod	4500	4	Clams			Crustacean larvae		
SeaStar	32000	4	Algae			Phytoplankton		
Crab	247	4	Decapod	10000	4	Polychateslarvae		
Mysid			Mussels	1200	2	Echinoderms	1700	7
Shrimp	1560-2450	4	Pelecypod	57000	4	Gastropod larvae		

Contaminant's Name			***COPPER***			Polychates	200	4
Molluscs	400-20000	5-30	Gastropod	58	4	SeaUrchin	300	
Bivalve			Oyster	35-45	6	Crustaceans	100-250000	4
Copepod	40-60	4	Clams	570	4	Crustacean larvae	48-170	4
SeaStar			Algae	10-15	1-2	Phytoplankton		
Crab			Decapod	250000-1	4	Polychateslarvae	180	4
Mysid			Mussels	200	4	Echinoderms		
Shrimp	146-250	4	Pelecypod			Gastropod larvae	110	2
Rotifer	43-84	1	Annelids			Amphipod	1250	4

Contaminant's Name			***LEAD***			Polychates	6800	4
Molluscs	4400-4520	7	Gastropod			SeaUrchin		
Bivalve	8800	7	Oyster	380-550	2	Crustaceans	580	4
Copepod	484-876	4	Clams			Crustacean larvae		
SeaStar			Algae	3110-794	10-14	Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels	10000	2	Echinoderms		
Shrimp	3130	4	Pelecypod			Gastropod larvae		
Rotifer	>4000	1	Annelids	840-7550	28	Amphipod	14100	4

Contaminant's Name			***MERCURY***			Polychates	22	4
Molluscs	4.0-5070	5-12	Gastropod	32000	4	SeaUrchin		
Bivalve	58-400	4	Oyster			Crustaceans	50-230	4
Copepod	8-12	4	Clams			Crustacean larvae	8.2-17	4
SeaStar	60	4	Algae			Phytoplankton		
Crab			Decapod	10-156	2	Polychateslarvae	100	4
Mysid			Mussels			Echinoderms	20	7
Shrimp	250	2	Pelecypod	1000	37	Gastropod larvae		
Rotifer	59-62	1	Annelids	17-90	7-28	Amphipod		

Contaminant's Name			***m-XYLENE***			Polychates		
Molluscs			Gastropod			SeaUrchin		
Bivalve	235000	3	Oyster			Crustaceans	3200-33000	
Copepod	215000	4	Clams			Crustacean larvae		
SeaStar			Algae	400000	1	Phytoplankton		

Crab	170000	2	Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	21400	4	Pelecypod			Gastropod larvae		

Contaminant's Name			*NAPTHALENE*			Polychates	3500-4100	4
Molluscs	57000	4	Gastropod			SeaUrchin		
Bivalve	57000	4	Oyster			Crustaceans	850-5700	2-4
Copepod	67800	4	Clams			Crustacean larvae		
SeaStar			Algae	<695	11-14	Phytoplankton		
Crab	>2000	4	Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	451280	4	Pelecypod			Gastropod larvae		
Rotifer			Annelids	3800	4	Amphipod		

Contaminant's Name			*NICKEL*			Polychates		
Molluscs			Gastropod	72000	4	SeaUrchin		
Bivalve	1200	4	Oyster			Crustaceans		
Copepod	6000	4	Clams			Crustacean larvae		
SeaStar	150000	4	Algae			Phytoplankton		
Crab			Decapod	47000	4	Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	387-635	4	Pelecypod			Gastropod larvae		
Rotifer	>20000	1	Annelids	154000-5	7	Amphipod	40000	10

Contaminant's Name			*PENTACHLOROPHENOL*			Polychates	435	4
Molluscs	163-18000		Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	70-10000	
Copepod	126	2	Clams	250	4	Crustacean larvae		
SeaStar			Algae	32	100	Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels	750	14	Echinoderms	710-870(EC	2
Shrimp	9500	14	Pelecypod			Gastropod larvae		
Rotifer	7610	4	Annelids			Amphipod	90	2

Contaminant's Name			*SELENIUM*			Polychates		
Molluscs	255-2000	86hr	Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	738-82000	2-3
Copepod	1700-2500	4	Clams			Crustacean larvae		
SeaStar			Algae	1000(EC5	3	Phytoplankton		
Crab	28400-382	4	Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	600	4	Pelecypod			Gastropod larvae		
Rotifer	6000-2800	1	Annelids			Amphipod		

Contaminant's Name			***SILVER***			Polychates		
Molluscs			Gastropod			SeaUrchin		
Bivalve			Oyster	25	12	Crustaceans		
Copepod	43	4	Clams	116-208	8	Crustacean larvae		
SeaStar			Algae			Phytoplankton		
Crab	55	1	Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	249	4	Pelecypod			Gastropod larvae		
Rotifer	120	1	Annelids			Amphipod		

Contaminant's Name			***THALLIUM***			Polychates		
Molluscs			Gastropod			SeaUrchin		
Bivalve			Oyster			Crustaceans	2130-10000	4
Copepod	2400	2	Clams			Crustacean larvae		
SeaStar			Algae	330(EC50	5	Phytoplankton		
Crab			Decapod			Polychateslarvae		
Mysid			Mussels			Echinoderms		
Shrimp	2500	2	Pelecypod			Gastropod larvae		
Rotifer	18.8umol/l	1	Annelids			Amphipod		

Contaminant's Name			***ZINC***			Polychates	3500-10700	4
Molluscs	15000-275	4	Gastropod	50000	4	SeaUrchin		
Bivalve	2500-4300	4	Oyster			Crustaceans	400-13000	4
Copepod	1450	4	Clams			Crustacean larvae	180-1200	4
SeaStar	>10000	4	Algae	13-796	5-10	Phytoplankton		
Crab			Decapod	9500-131		Polychateslarvae	1700	4
Mysid			Mussels	175	2	Echinoderms	>10000-390	4
Shrimp			Pelecypod	2500-430	4	Gastropod larvae		
Rotifer			Annelids			Amphipod	580	4