DRILLING WASTE DISCHARGES IN THE MARINE ENVIRONMENT: A RISK BASED DECISION METHODOLOGY

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0-612-73562-1

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by

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A Thesis submitted to the Graduate Studies
in partial fulfilment of the requirement for the degree
of Doctor of Philosophy

Faculty of Engineering and Applied Science

Memorial University of Newfoundland

December, 2001

St. John's Newfoundland Canada

ABSTRACT

Offshore drilling operations generate rock cuttings and spent drilling fluids wastes during the well drilling phase. The wastes contain toxic substances that are harmful to the marine ecosystem. Discharge limitations and restrictive guidelines in different jurisdictions of the world are under development. Pollution prevention by encouraging synthetic based fluids (SBFs) in place of traditional oil based fluids has been supported in recent years. Despite having environmentally benign characteristics, SBFs associated wastes still have a certain amount of pollutants due to barite and contamination with formation oil.

The main aim of this study was to develop a risk management framework for determining the best drilling waste discharge scenario for disposal in the marine environment. The specific objectives of this research were: (1) development of probabilistic contaminant fate modeling methodology using fugacity and aquivalence based approaches; (2) development of an ecological risk assessment methodology using probabilistic concepts; (3) development of human health cancer and non-cancer risk assessment methodologies using probabilistic concepts; (4) development of a fuzzy composite programming framework for risk management by integrating environmental risk, cost estimates and technical feasibility for various treatment options; and (5) an application of the developed risk management framework to a hypothetical case study.

Fate modeling in this research was performed using fugacity and aquivalence based concepts. A chemical specific approach was employed for contaminant fate modeling. A steady state non-equilibrium water and sediment interaction model with probabilistic inputs was used to determine the contaminant concentrations in the water column and pore water. The uncertainty and variability in the model inputs were expressed by the statistical distributions. The concentrations in the water column and pore water were estimated using Latin Hypercube sampling (LHS) based Monte Carlo (MC) simulations. The concentrations in the water column and pore water followed lognormal distributions. The estimated parameters of lognormal distribution for known discharge conditions were used for performing multiple regression analyses. The highest 95th percentile was used as the predicted environmental concentration (*PEC*). The uncertainties in the *PEC* were expressed by the coefficients of regression models.

The *PEC* values were converted into exposure concentrations (*EC*) by adjusting for bioavailability and probability of exposure. The whole ecological community was defined as assessment endpoints. The toxicity assessment analyses were based on the lognormally distributed predicted no effect concentrations (*PNEC*). The lowest 10th percentile on *PNEC* distributions was used as a safety level or *PNEC* criteria value. Bootstrapping was performed on original *PNEC* data to determine the uncertainty in the *PNEC* criteria values. The hazard or risk quotients (*HQ/RQ*) were calculated by dividing *EC* with *PNEC* criteria values. The CHARM model's approach was used to convert *HQ/RQ* into risk estimates for each contaminant. The composite ecological risk for drilling waste was determined by integrating the individual risk estimates assuming statistically independent events.

The human health risk methodology was based on the consumption of contaminated seafood. A probabilistic framework for human health risk assessment was developed for cancer and non-cancer risk estimates. The chronic daily intake rate (*CDI*) was established based on fish ingestion rates, lipid content, bioconcentration factors, exposure duration, exposure frequency, and averaging time. The LHS based MC simulations were performed to estimate the *CDI*. Arsenic was the only proven human carcinogen in the drilling waste stream. The composite hazard index for non-cancer risks was calculated by simple addition for a given exposure scenario.

A risk management methodology using fuzzy composite programming (CP) was developed. The costs for treatment, drilling fluid loss due to discharge and ecological and human health damages were estimated. The technical feasibility of various solid control devices was also studied from a performance viewpoint. The environmental risk reductions, cost saving and technical feasibility indices were grouped using CP methodology. A double weighting scheme was employed in CP. The final utility and centroidal values of the system improvement indices were calculated through Chen and Yager fuzzy ranking methods, respectively to determine the best management alternative.

The risk management framework was applied to a hypothetical case study on the East Coast of Canada. Five discharge scenarios, or management alternatives including 10.0%, 8.5%, 7.0%, 5.5% and 4.0% attached base fluids to wet cuttings, were selected for the analysis. The 4% attached base fluid option was found to be the best management option for the first trial when risk and cost were given equal weight and technical feasibility was allotted one-third of the weight. The 7.0% discharge option was the second best management option and that was followed by the 5.5%, 8.5% and 10.0%, respectively. The sensitivity analysis was performed using four different weighting schemes to account for human subjectivity. It was concluded that 4.0% was the best management alternative for the discharge of drilling waste in the marine environment. The other better management alternatives were the discharge options of 7.0% and/or 5.5% attached base fluid to the wet cuttings (approximately 5 - 6% of dry cuttings).

This study has introduced a new concept of integrating probabilistic fate modeling with ecological and human health risk assessment methodologies within a risk management framework to determine the best management alternative under conflicting objectives. This study has provided a framework for a decision support system for the selection of the best drilling waste marine discharge option under any known regulatory and technical constraints.

ACKNOWLEDGEMENTS

Praise and thanks be to *Allah Almighty*, the most Gracious, the most Merciful, and Peace and Blessing of *Allah Almighty* be upon *His Prophet* (SAW).

First, I would like to thank my wife Bushra for her love and support during the course of this research. I am also greatly indebted to my mother, brothers Gul and Khayyam, and sister Shazia for their continuous support.

Many thanks are extended to my supervisors Dr. Tahir Husain, Dr. Brian Veitch and Dr. Neil Bose for their guidance, help and support.

I thank the Faculty of Engineering and Applied Science, Memorial University of Newfoundland (MUN), ACOA and NSERC strategic project (Offshore Environmental Engineering Using Autonomous Underwater Vehicles) for their financial support.

Finally, I would like to thank my friends in MUN, Amir, Aman, Faisal, Anis bhai, Nad, JP, Mukhtasor, Ejaz, Kamaran, Mansoor and Gatot for providing me with a pleasant and friendly living and healthy working environment.

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α	Regression Coefficients
A	Aquivalence or Coefficient for Deposition
A_i	Management alternatives
A_w	Impact Area
B	Bias Correction Factor or number of bootstrap samples
C	Concentration
C_E	Effluent Concentration
C_{PW}	Concentration in Pore Water
C_W	Concentration in Water Column
δ	Grain/Particle Diameter
D	Transportation or Transformation Parameter
Δ	Sediment Mixing Depth
D_{BW}	Diffusion Coefficient
d_w	Depth of Water Column
E	Pollutant Loading Rate
E	Exponential Distribution

ε	Error Term or Resuspension Rate (mg/m^2-hr)
EC_{50}	Concentration at 50% Adverse Effects
f_i	Fugacity
Φ_i	Organic Fraction
Φ^{-1}	Standard Normal Function
Φ_{max}	Scalar Corresponding to the Maximum Eigen Value
G	Gibbs's Free Energy
G	Gravity Force
G_t	Flow Rate
g	Gibbs's Free Energy/mole
h	Enthalpy or membership value
H	Henry's Law Constant (Pa. m^3/mol)
$H_{1/2}$	Half Life
i	Discount Rate
k	Rate Constant
K_{AW}	Air-Water Partitioning Coefficient
K_B	Bioconcentration Factor (*BCF*)
K_{OC}	Portioning Coefficient for Organic Carbon
K_{OW}	Octanol Water Partitioning Coefficient
K_P	Portioning Coefficient (L/kg)
K_π	Sediment Partitioning Coefficient
K_σ	*SS* Partitioning Coefficient
K_{SW}	Water-Sediment Partitioning Coefficient
L_r	Lipid Content
LC_{50}	Lethal Concentration to Kill 50% of Organisms
$L_{fh}(x)$	Index Value at Membership Function of *h*
LN	Lognormal Distribution
m	Mass
μ	Mean
μ_h	Membership Function
n	Molar Concentration

N	Normal Distribution
P	Pressure
p	Probability
P2	Pollution Prevention
p_j	Balancing Factor
PW	Pore Water (Subscript)
R	Impact Radius or Universal Gas Constant
ρ	Density
R^2	Coefficient of Determination
ρ_r	Rank Correlation Coefficient
s	Entropy
S	Solubility
σ	Standard Deviation
t	Time
T	Temperature
T	Triangular Distribution
TN	Truncated Normal Distribution
τ	Shear Stress
U	Uniform Distribution
u	Advective Velocity or Current Speed
u_β	Burial Rate
U_i	Intermedia Transport Velocities
$U_i(x)$	Utility Value
v	Volume Fraction
V	Volume
w	Settling Velocity
$w_{i,j}$	Weight Reflecting Importance of Basic Indicator
W	Water (Subscript)
ξ	Resuspension Coefficient
Z	Fugacity Capacity
Z'	Aquivalence Capacity

LIST OF ACRONYMS

AHP	Analytical Hierarchy Process
API	American Petroleum Institute
ASTM	American Standard for Testing and Materials
AT	Averaging Time
Aus-NZ WQG	Australia-New Zealand Water Quality Guide Lines
BAT	Best Available (economically achievable) Technology
bbl	Barrels (160.4 L)
bblt	Benthic Boundary Layer Transport
BCF	Bioconcentration Factor
BCT	Best Conventional Pollutant Control Technology
BF	Bioavailable Fraction
BI	Bootstrap Interval
BPT	Best Practicable Control Technology
BW	Body Weight
CCME	Canadian Council of Ministers for Environment
CDF	Cumulative Distribution Function
CDI	Chronic Daily Intake (mg/kg-day)
CF	Conversion Factor
CHARM	Chemical Hazard Assessment and Risk Management
CI	Confidence Interval
CM	Control Measures
CNOPB	Canada-Newfoundland Offshore Petroleum Board
CP	Composite Programming

CPI	Consumer Price Index
CWA	Clean Water Act
DC	Dry Cuttings
DF	Dilution Factors
EC	Exposure Concentration
ED	Exposure duration
EDF	Empirical Distribution Function
EF	Exposure Frequency
EIA	Environmental Impact Assessment
EMO	Enhanced Mineral Oil
EO	Ease of Operation
EqP	Equilibrium Partitioning Approach
FIR	Fish Intake Rate
FPSO	Floating Production and Offloading System
FRU	Fine Removal Unit
GBS	Gravity Based Structure
GM	Geometric Mean
GoF	Goodness of Fit
GOM	Gulf of Mexico
GWI	Global Warming Impact
H&S	Health and Safety
HHRA	Human Health Risk Assessment
HI	Hazard Index
HIc	Composite Hazard Index
HQ	Hazard Quotient
IA	Iso-Alkane
IO	Internal Olefins
IR	Intake Rate
IRIS	Integrated Risk Information System
JUV	Joint Uncertainty and Inter-individual Variability
LAB	Linear Alkyl Benzene

LAO	Linear Alpha Olefins
LCA	Life Cycle Analysis
LF	Leaching Factor
LHS	Latin Hypercube Sampling
LOEC	Lowest Observed Effect Concentration
MADM	Multiple Attribute Decision-Making
MAUF	Multiple Attribute Utility Function
MATC	Maximum Acceptable Toxicant Concentration
MC	Monte Carlo (simulations)
MCDM	Multiple Criteria Decision-Making
MLV	Most Likely Value
MMS	Minerals Management Service
MODM	Multiple Objective Decision-Making
MSDS	Material Safety Data Sheet
MT	Mass Transfer Coefficient or Metric Tones
MW	Molecular Weight
NGL	Natural Gas Liquid
NOEC	No Observed Effect Concentration
NORM	Naturally Occurring Radioactive Materials
OBF	Oil Based Drilling Fluid
ODP	Ozone Depletion Potential
OOC	Offshore Operator's Committee
OSPAR	Oslo and Paris
PAHs	Polynuclear Aromatic Hydrocarbons
PAO	Polyalpha Olefins
PCBs	Polychlorinated Biphenyls
PDF	Probability Density Function
PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration
PSS	Primary Shale Shaker
QSAR	Quantitative Structure Activity Relationship

QWASI	Quantitative Water Air Sediment Interaction
RfD	Reference Dose
RMS	Root Mean Square
RMSE	Root Mean Square Error
ROC	Retention on Cuttings
RQ	Risk Quotient
SA	Sensitivity Analysis
SAW	Simple Additive Weighting
SBF	Synthetic Based Drilling Fluid
SE	Standard Error
SF	Slope Factor
SS	Suspended Solids
SS_i	Sum of Squares
SSS	Secondary Shale Shaker
ST	Status of Technology
TW	Total Weight
U.S. DOE	U.S. Department of Energy
U.S. EPA	United States Environmental Protection Agency
UF	Uncertainty Factors
WBF	Water Based Drilling Fluid

Chapter 1

INTRODUCTION

This research was planned to integrate and apply various components of risk-based decision methodology for synthetic based drilling waste discharges in the marine environment. The components of this risk-based approach are contaminant fate modeling, ecological and human health risk assessment and risk management. This thesis focuses on all these components of risk-based decision-making approach with relevance to drilling waste discharges in the marine environment. A hypothetical case study is also discussed in this thesis for an application of the developed holistic methodology.

1.1. BACKGROUND OF THE RESEARCH

Demand for energy sources is increasing throughout the world at a rapid rate due to industrial development and population growth. This increasing demand has accelerated the search for new sources of oil and gas on land and offshore. Oil production involves two main phases of drilling operations, namely exploration and development. The exploration phase operations determine the potential hydrocarbon reserves and include drilling of exploratory wells, whereas the development phase operations include drilling of production wells, once a hydrocarbon reserve has already been discovered and delineated. The rigs used in exploration and development sometimes differ but the drilling process is generally the same for both types of operations (U.S. EPA. 1999a).

Drilling operations use drilling muds to lubricate the drill bit. control borehole pressure. and flush rock cuttings out of the well. Disposal of rock cuttings and used mud constitutes one of the most significant waste discharges associated with offshore drilling. The drilling fluids or circulating muds. are broadly classified into three groups (U.S. EPA. 1999a).

- Water based drilling fluid (WBF): conventional drilling mud with water used as its continuous phase.
- Oil based drilling fluid (OBF): diesel. mineral. or some other oil used as its continuous phase.
- Synthetic based drilling fluid (SBF): synthetic based material like polyesters and vegetable esters used as its continuous phase.

SBF consists of a synthetic base fluid. weighting agent (barite) and some other additives. Since 1990. the oil and gas extraction industry has developed many synthetic and non-synthetic materials as base fluids to provide drilling performance characteristics comparable to traditional oil based fluids (OBFs) with the lower environmental impacts and greater worker safety of water based fluids (WBFs). These characteristics have been achieved through lower toxicity. elimination of polynuclear aromatic hydrocarbons

(PAHs), faster biodegradation rates and lower bioaccumulation potential of pollutants (U.S. EPA, 1999a).

Prohibition of the discharge of rock cuttings into the North Sea has been implemented (U.S. EPA, 2000a). As a result, all cuttings must now be either re-injected downhole, or shipped to the shore for treatment and disposal. The regulatory authorities in Nova Scotia have effectively followed suit, moving from a relatively lax 15% (by dry weight) drilling muds on cuttings allowed at discharge to 1%. As the best available economically achievable technology (BAT) can reduce contaminants to the neighbourhood of 4% (U.S. EPA, 2000a), the 1% allowable limit is in practice a prescription of a total ban on drilling waste discharges.

The United States Environmental Protection Agency (U.S. EPA) has identified different options to reduce the discharge of drilling waste into the marine environment. Current industry practice for managing and treating SBF-cuttings before discharge is to process the cuttings through solids separation equipment, which consists of primary and secondary shale shakers and occasionally a centrifuge. Based on current industry data, the efficiency of solids separation equipment results in a long-term average of 10.2% (by wet weight) retention on cuttings. By using new treatment technology, the retention of fluids can be reduced to approximately 4% (U.S. EPA, 2000a, b).

The disposal of drilling fluids into the ocean environment is of major concern for two main reasons: economical loss associated with discharged expensive synthetic drilling fluids with rock cuttings and probable adverse ecological impacts. To determine the fate of contaminants associated with drilling waste, several studies have been conducted in the past. The U.S. EPA (2000a) developed a methodology for assessing surface water and pore water quality impacts by using the Offshore Operator's Committee (OOC) model as described by Brandsma (1996). In this analysis it was assumed that discharged contaminants immediately leached into the water column or into the pore water. Instead of SBFs waste as a whole, constituent organic priority pollutants and heavy metals were studied in this analysis. Some other modeling attempts have been conducted based on particle tracking techniques (e.g., Seaconsult, 2000). A set of models for the dispersion and drift of drilling wastes and suspended sediment in the benthic boundary layer is being developed by Hannah et al. (1997) who applied these models to the Georges Bank, Canada.

Thibodeaux et al. (1986) developed a model for the fate and transport of chemical contaminants originating from offshore drilling bottom deposits. This model was limited to the transport of the soluble constituents from the cuttings and mud deposits. This model does not take into account particulate transport and chemical and biochemical transformations that degrade contaminants within the sediment zone or boundary layer. In the North Sea OSPAR (Oslo and Paris), the Chemical Hazard Assessment and Risk Management (CHARM) model was developed to help stakeholders, including regulators, operators and chemical suppliers. The CHARM model includes a risk management module (Thatcher et al., 1999). This model categorises wastes into different application groups, such as production waters and WBFs. The OBFs are not addressed in this model due to limited information on input parameters such as biodegradation and bioaccumulation characteristics.

Mackay developed a methodology for estimating chemical fate in multimedia based on the complexity of transport and transformation processes. Mackay and co-workers (1983, 1989 and 1994) applied a fugacity/aquivalence model called QWASI (Quantitative Water Air Sediment Interaction) to rivers, lakes and Hamilton harbour, to study the distribution of detergent chemicals, PCBs (Polychlorinated biphenyls) and heavy metals. In principle, the concept can be applied to any well-mixed body of water for which hydraulic and particulate flow characteristics are defined. QWASI is a steady state non-equilibrium model, which is generally used in the deterministic mode so uncertainties associated with the input variables are not addressed.

Synthetics based fluids (SBFs) are hydrophobic in nature and tend to sink to the bottom with little dispersion. Therefore, the main research focus has been on determining toxicity in the sedimentary phase as opposed to the aqueous phase. Many studies including Candler and Leuterman (1997) and Rabke and Candler (1998) have reported the toxicity response of SBFs for different organisms. In addition to the toxicity of the base fluid, the drilling waste contains organic priority pollutants and heavy metals, which adversely affect the ecological community (U.S. EPA, 1999a). The CHARM model calculates ecological risk by taking the ratio of two parameters: the predicted environmental concentration to the predicted no effect concentration (*PEC/PNEC*). This method is similar to the U.S. EPA approach where predicted concentration is compared with Federal Water Quality Criteria (U.S. EPA, 1999b).

Another aspect of environmental risk assessment of drilling waste is human exposure through consumption of contaminated commercial fish. Marine organisms are exposed to pollutants through direct uptake (bioconcentration) and consumption of lower trophic level organisms (biomagnification). Bioaccumulation of chemicals in aquatic food chains, which is a combined effect of the above two processes, is an important phenomenon in aquatic organisms and affects their predators, especially humans and fish-eating wildlife (Campfens and Mackay, 1997). The consumption of contaminated organisms may pose a threat to human health. A deterministic analysis for human exposure and related non-carcinogenic and carcinogenic health risk through consumption of finfish and shrimps is given by the U.S. EPA (1999b, 2000a).

Cost comparisons of different discharge options for water quality, and in the case of zero discharge the non-water quality environmental impacts, are provided in the U.S. EPA study (2000a). The risk management module of the CHARM model is not well accepted by stakeholders, although it compares various alternatives for risk reducing measures. The basis of risk management in the CHARM model is to combine the risk of individual substances into a single risk estimate. The several management alternatives can be compared on the basis of their cost and risk reduction strategy. Some other researchers (e.g. Stansbury et al., 1989) used composite programming for management of dredged material, which accommodated conflicting objectives of environmental risk and cost in their analysis.

To fill in the gap in the scientific literature for managing disposal of drilling waste in the marine environment, a risk-based approach was used. This research integrated contaminant fate modeling, and ecological and human health risk assessment based on risk management methodologies (Sadiq, 2000).

1.2. SCOPE AND PURPOSE OF THE RESEARCH

The study had the following major objectives: determining the fate of contaminants in the water column and the sediment pore water; developing methodologies for ecological and human health risk assessments; and incorporating those in a risk management framework that could also evaluate various treatment technologies using a case study. The pollutant discharged was characterised by considering regulations proposed by different regulatory agencies including the Canada-Newfoundland Offshore Petroleum Board (CNOPB), U.S. EPA and Norwegian Pollution Control Authority (SFT).

The steady state probabilistic model for partitioning of contaminants in multimedia was developed using fugacity/aquivalence approaches. The multimedia-partitioning model was integrated with an Environmental Risk Assessment methodology, which helped to decide the best management strategy for the discharge of drilling wastes. Probabilistic and fuzzy arithmetic concepts were incorporated throughout the modeling process to account for uncertainties.

In this research, a methodology for probabilistic contaminant fate modeling was proposed, which was integrated with environmental risk assessment and risk based multiple criteria fuzzy composite programming. To accomplish the above objectives, the proposed research covered the following tasks:

- Development of a methodology for fate modeling using probabilistic concepts;
- Development of a methodology for ecological risk assessment;
- Development of a methodology for human health risk assessment;
- Development of a risk based decision-making approach by incorporating human health and ecological risks, technical feasibility of various treatment options, and environmental damage and treatment costs; and
- Application of developed methodologies for a hypothetical case study.

The following are some environmental issues related to offshore drilling waste discharges, which were not studied in this research.

- Non-water quality environmental impacts, which include greenhouse gases and other air pollution problems;
- The drilling fluid exposure to workers during handling and treatment and their related health risk; and
- The ecological damages caused by smothering and burial by drill cuttings.

1.3. ORGANIZATION OF THE THESIS

This thesis is comprised of eight chapters. The first two chapters provide an introduction to the problem and establish the theoretical background of the problem. Chapters 3-6 are mainly methodology-based chapters, which discuss relevant literature during the course of developing models. Chapter 7 is an application-based chapter and uses models and methodologies developed in previous chapters for a hypothetical case study. Conclusions and recommendations of this research are presented in Chapter 8. Figure 1.1 explains the organization of this research (Sadiq, 2000).

Specifically, Chapter 1 explains the scope and objectives of the research and the organisation of the thesis. Chapter 2 covers the theoretical background of the research and provides information about characteristics of drilling waste, and different available approaches and models for contaminant fate modeling. The main focus of Chapter 2 is to discuss the background literature related with contaminant fate modeling.

Chapter 3 develops the proposed methodology for probabilistic fate modeling. Physico-chemical characteristics of contaminants and media (water column and sediments) are discussed in detail in this chapter. Based on probabilistic fate modeling results, regression models are developed in this chapter.

Chapter 4 develops a methodology for ecological risk assessment due to toxicological effects of chemicals present in the drilling waste. This analysis was performed based on U.S. EPA (1998) and Canadian Council of Ministers for Environment (CCME, 1997) ecological risk assessment frameworks. The components of an ecological risk assessment framework include problem formulation, an analysis phase and risk characterization, which are discussed in detail in this chapter with reference to drilling waste discharges. A probabilistic approach using Monte Carlo (MC) simulations was employed in this chapter.

Chapter 5 develops a methodology for human health risk assessment due to consumption of contaminated commercial fish. The input parameters for cancer risk and non-cancer risk models and the associated uncertainties are discussed in detail. A probabilistic approach using MC simulations was used to estimate the human health risk.

Chapter 6 develops a risk management methodology based on fuzzy composite programming. Literature related to risk management using multiple criteria decision-making methodologies is discussed. Various solid control treatment technology options available offshore are explored in this chapter. Cost estimations of treatment options, drilling fluids and environmental damage costs are also discussed. A risk management methodology was proposed by integrating risk estimates from chapters 4 and 5, and technical feasibility and cost estimates from Chapter 6.

Chapter 7 is a hypothetical case study on the East Cost of Canada. The models developed in the methodology-based chapters are applied in this case study. In this chapter various discharge scenarios are identified and pollutant loading rates are estimated based on available information.

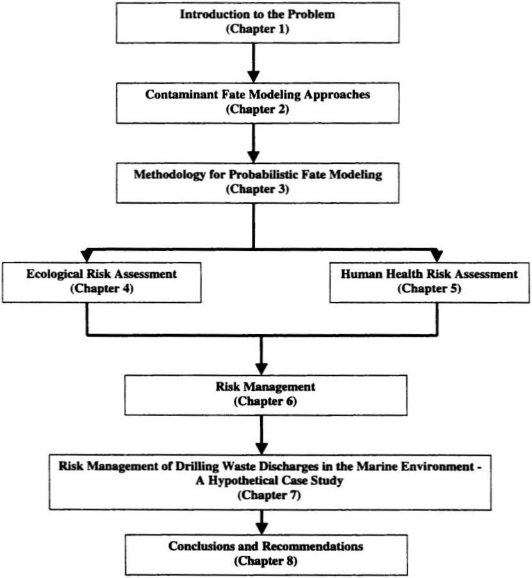


Figure 1.1. Organization of the thesis

Based on the estimated pollutant loading rates, contaminant concentrations are calculated in the water column and pore water using the regression models developed in Chapter 3. Based on exposure concentrations, ecological risks are characterized using the methodology developed in Chapter 4. The concentration in fish tissues are estimated based on contaminant exposure concentrations. Human health risks are estimated based on consumption of contaminated fish as discussed in Chapter 5. Cost estimates of treatment options for various discharge scenarios are made based on the methodology developed in Chapter 6. Assumptions are made for the missing information and data where necessary for a hypothetical case study. Comparisons of various discharge scenarios are discussed in detail in Chapter 7.

Chapter 8 discusses the conclusions from this research. Recommendations for the directions of future research are established based on the results obtained.

Chapter 2

POTENTIAL CONTAMINANT FATE MODELING APPROACHES

2.1. INTRODUCTION TO OFFSHORE OIL OPERATIONS

Various types of processing systems, equipment and operating techniques are used by the oil industry to explore, develop, and produce oil and gas from an offshore field. Operations during both the exploratory and development drilling stages also determine the design needs for offshore environmental considerations. Rotary drilling uses a system of circulating drilling fluid primarily to remove drill cuttings from the borehole. The drilling fluid cools and lubricates the drill string and drill bit; builds an impermeable cake on the well bore; controls subsurface pressure; supports part of the weight of the drill string; reduces the damage to the formation and conducts geological information from the formation to the surface (Meinhold, 1998).

The drilling fluid (mud) is a mixture of water, base fluids, special clays, and minerals and chemicals. The drilling fluid is pumped downhole through the drill string and is ejected through nozzles in the drill bit at high pressure. The jet of fluid lifts the cuttings off the bottom of the hole and away from the bit. The drilling fluid is circulated to the surface through the annulus between the drill string and casing. At the surface, the drill cuttings, silt, and sand are removed from the drilling fluid before it is returned downhole through the drill string. Figure 2.1 presents a schematic flow diagram of a drilling fluid circulation system.

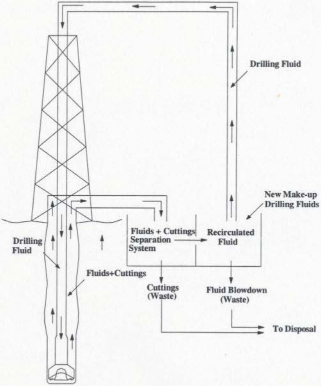


Figure 2.1. Typical drilling fluids circulation systems (U.S. EPA, 1999a)

The cuttings, sand, and silt are separated from the drilling fluid by a solid separation process. Some of the drilling fluid remains attached to the cuttings after treatment. After solid separation, the cuttings are disposed of in a manner that depends on the type of drilling fluid used, the oil content of the cuttings, and the regulatory regime. The disposal methods include transport to shore for land-based disposal, ocean discharge, and subsurface injection. A typical solids control system consists of some of the following equipment, depending on the drilling program: primary and secondary shale shakers to perform the initial separation of drill cuttings and fluid, and a centrifuge to remove drilling fluid from the waste stream. Figure 2.2 illustrates the arrangement of such a system.

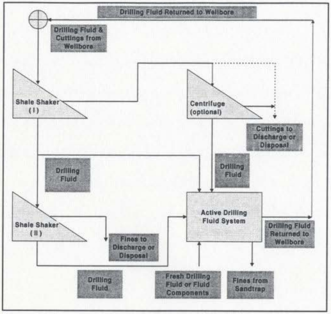


Figure 2.2. A layout of solid control system

2.2. DRILLING FLUIDS AND ASSOCIATED DRILLING WASTE

An OBF is a drilling fluid that consists of brine (seawater) contained as an emulsion in oil. This is in contrast to water based fluid (WBF), which consists of small quantities of oils present as lubricants as an emulsion within brine. Oil based fluids have been formulated with diesel and mineral oil. When shale is drilled with an OBF, the oil is in contact with the shale and the fine nature of the shales prevents entry of oil and the integrity of the shale is maintained. Therefore, reduction in shale water content occurs due to osmotic forces which leads to a strengthening of the shale in the near wellbore region. In contrast, when WBF is used to drill shale, water transmits from the fluid into the water-wet shale. The support of the shale is thus lost and the shale can washout of the wellbore (Hall, 2000).

Another characteristic of mineral oils is their high degree of natural lubricity. This is of great importance when drilling deviated and extended reach wells because drag factors are reduced and consequently so is the risk of the drill pipe becoming stuck. In contrast to WBF, the lack of polarity of the continuous phase of an OBF means that the fluids do not react with other potentially troublesome formations, such as salt, gypsum, and anhydrite. Mineral oils also provide stable mud properties over a wide range of temperatures and hole conditions and have corrosion inhibiting properties (Meinhold, 1998).

OBF shows poor biodegradability in aerobic conditions and the degradation of mineral oils is extremely slow in anaerobic conditions, which are the typical conditions found within a drill cutting pile. The U.S. EPA's initial legislation limiting discharge of oil or diesel based drilling fluid attached set a maximum of 15% of the total wet weight of cuttings discharged to the seafloor. This has led to a legacy of drill cutting piles, whose physico-chemical properties have not appreciably changed since they were deposited 15 to 20 years ago, due to slow biodegradation rates (Hall, 2000).

The discharge of oil-contaminated cuttings during drilling activity is one of the major contributors to oil industry impacts upon the marine environment. The early focus of efforts to reduce the environmental impacts was centered on reducing the volumes of drilling fluids discharged with the cuttings, as well as the generic toxicity of the base oil itself. By 1985 it became clear that regardless of the inherent levels of toxicity of the base oils, the cuttings piles persisted and continued to pollute for many years due to leaching of chemicals into the ambient environment (Hall, 2000).

The U.S. EPA (1999b) suggested product substitution (e.g., SBFs instead of OBFs) as the best way of reducing offshore oil environmental impacts. The oil and gas extraction industry has developed many oleaginous (like oil) base materials such as vegetable esters, poly-alpha olefins (PAO), internal olefins (IO), linear alpha olefins (LAO), iso-alkane (IA), ethers, linear alkyl benzene (LAB), and others to increase the efficiency of drilling operations. These base fluids were developed to obtain the drilling performance of traditional OBFs in addition to lower environmental impact potential. The wastes generated from SBFs are less toxic, have lower bioaccumulation and faster biodegradation potential, and are free of polyaromatic hydrocarbons (PAHs). Table 2.1 gives a comparison of the PAH content of SBFs and OBFs. A lower PAH implies lower toxicity to an ecological community.

Table 2.1. PAH content comparison of SBFs and OBFs (modified after Meinhold. 1998)

Base Fluid	PAH (%)	
Diesel	25	**OBFs**
Conventional mineral oil	1 - 7	
Paraffin oil	<1	
Enhanced mineral oil (EMO)	0.001 - 0.2	
Esters	≈ 0	**SBFs**
Acetal	≈ 0	
Poly-alpha olefins (PAO)	≈ 0	
Linear alpha olefins (LAO)	≈ 0	
Iso-alkane (IA)	≈ 0	
Internal olefins (IO)	≈ 0	

With these improved characteristics, the U.S. EPA (1999a) is still proposing a controlled discharge of the cuttings associated with SBFs. SBFs are less dispersible in nature and sink to the seafloor, and may be a potential environmental concern to the benthic community. It is believed that environmental impacts include smothering by the drill cuttings, changes in grain size and composition, and anoxia caused by the decomposition of organic matter (U.S. EPA, 1999a). The environmental impacts associated with the zero discharge of OBFs can be more harmful than the discharge of SBFs due to non-water quality environmental impacts, like air pollution and ground water pollution in the case of incineration and land based disposal, respectively (U.S. EPA, 1999a). A qualitative comparison of OBFs, WBFs and SBFs for various offshore/onshore activities is given in Table 2.2. Various environmental factors are ranked from scale 0 to 3. A bigger value represents the higher risk potential involved in that activity (or factor).

Table 2.2. A qualitative comparative assessment for drilling fluids in different activities (modified after Meinhold, 1998)

Activity	Risk Type	Factors	OBFs	WBFs	SBFs
Drilling	Occupational	Accidents	2	3	2
		Chemical exposure	2	1	1
	Public	Air emissions	1	2	1
	Environmental	Air emissions	1	2	1
		Spills	2	1	1
	Energy use		1	2	1
Onsite discharge/ solids control	Occupational	Accidents	2	1	1
		Chemical exposure	2	1	1
	Public	Bioaccumulation and ingestion	0	1	0
	Environmental	Water column effects	0	1	0
		Bioaccumulation and effect	0	1	0
		Benthic effects	1	1	1
	Energy use		1	1	1
Loading and transportation	Occupational	Accidents	3	0	1
		Chemical exposure	2	0	1
	Public	Air emissions	1	0	0
		Accidents	1	0	1
	Environmental	Spills	3	0	1
		Water emissions	1	0	0
		Air emissions	2	0	0
	Energy use		2	0	0
Onshore disposal	Occupational	Accidents	3	0	0
		Chemical exposure	2	0	0
	Public	Air emissions	2	0	0
		Groundwater contamination	1	0	0
	Environmental	Air emissions	2	0	0
		Groundwater contamination	1	0	0
	Energy use		2	0	0
Resource impacts (Landfill space/injection capacity)			2	1	0
Economic impacts			3	1	2
Liabilities			3	1	1

0: No risk because this activity is not involved or negligible value of risk is expected
1: Low value of risk
2: Medium value of risk
3: High value of risk

The volume of drill cuttings generated depends on the dimensions of the well and percent washout, the type of formation being drilled, the type of drill bit, and the type of drilling fluid used (Meinhold, 1998). The discharge of cuttings with adhering drilling fluids and additional minor quantities of attached fluids is not constant, as cuttings are discharged only during drilling periods. The amount of drilling fluids adhering to discharged cuttings and subsequently released from the waste treatment process is difficult to estimate in general, but the quantity of drilling fluid used is directly proportional to the depth of the well.

The Minerals Management Service (MMS, 1989) classifies wells based on the depth of the water column. The wells in water deeper than 300 m are called deep water wells. Wells in less than 300 m are shallow water wells. The U.S. EPA (2000a) studied three specific offshore areas: the Gulf of Mexico, California, and Alaska's Cook Inlet. The analysis was further categorised on the basis of current discharge practice (10.2% attachment of SBF to the rock cuttings) and two proposed discharge options (approximately 4%). The details of the quantities of attached drilling mud and expected drill cuttings for different model wells are summarised in Table 2.3 (U.S. EPA, 1999a, b).

Table 2.3. Summary for model wells (modified after U.S. EPA, 2000a)

Model Well	Hole Diameter (cm)	Depth Interval (m)	Volume of Cuttings (including 7.5% washout) (m^3)	Volume of 10.2% attached base fluid (m^3)
Shallow Development	22	2300	95	38.4
Shallow Exploratory	15-31	450-1825	190	80.4
Deep Development	22-31	600-1375	137	58.1
Deep Exploratory	22-45	600-1375	305	129.1

Research into alternative biodegradable base fluids started with common vegetable oils including oil from peanuts, rapeseeds and soya beans. Esters were found to be the most suitable naturally derived base fluids in terms of potential for use in drilling fluids. Esters are exceptional lubricants, show low toxicity and a high degree of biodegradation both aerobically and anaerobically. There are various fatty acids and alcohols from which esters can be synthesised. Following the success of esters, other drilling fluids were formulated that were classified as synthetics. These new products have not matched the environmental performance of ester based drilling fluids (Hall, 2000). A comparison of SBFs based on toxicity (LC_{50} - lethal concentration to kill 50% of organisms), potential for bioaccumulation (K_{OW}, octanol-water partitioning coefficient) and biodegradation under aerobic and anaerobic conditions is shown in Table 2.4. Higher values of LC_{50} show lower toxicity and smaller values of K_{ow} represent lower bioaccumulation potential. Some of the olefin fluids are still in use, but in many areas of the world their discharge on cuttings is being restricted because they do not show sufficiently good performance in terms of biodegradation and toxicity (Hall, 2000).

Another aspect of ester comparison with other synthetic based drilling fluids is the human contact with the drilling fluids during treatment and drilling operations. Skin contact occurs on the drilling floor, and it can also be inhaled through vapors in the shale shaker room. People working on the drill floor may have extensive contact with the drilling fluid and there is a potential danger of splash in the eyes. SBFs have higher boiling points and flash points and reduced vapor pressure than OBFs. SBFs vapors concentrations reported in the North Sea are less than 10 mg/m^3 (Meinhold, 1998). Table 2.5 presents occupational health data reported by drilling fluid manufacturers.

Table 2.4. Properties of synthetic based drilling fluids

Fluid Type	Year	Source	Carbon Atoms	Lethal Concentration (LC_{50} in mg/kg dry weight of sediment)[1]							K = $LogK_{ow}$ [2]	(%) [3] Aerobic Biodeg.	(%) [4] Anaerobic Biodeg.	Status
				10-d *LP* [a]		96-hr *LP* [b]		10-d *CV* [c]	*SC* [d] mg/L	*AC* [e] mg/L				
				U.S. EPA	Baroid (Hall, 2000)	U.S. EPA	Baroid (Hall, 2000)							
Esters	1989	Palm Kernel Oil	8 - 14	≈ 5700-10200	≈ 9900-10100	≈ 14300-22000	≈ 20,000	>10000	60000	50000	1.69	82	80	Usage increasing globally
PAO	1991	Natural Gas	20 - 30	>10000				>10000	3900	>50000	15.4	52	12	Poor Biodegradation
LAO	1992	Natural Gas	14 - 18	≈ 550-900	≈ 150-400	≈ 1000	≈ 150-1000	1270	>10000	>10000		72	20	Being increasingly regulated against
IO	1994	Natural Gas	15 - 18	≈ 1650-2500	≈ 350-650	≈ 1100-2900	≈ 350-2000		2050	>10000	>9.0	68	34	
IA[6]	Petro-Canada PUREDRILL IA-35		11- 21	>400,000 mg/L *Rainbow trout* (96-hr)		>1,000,000 mg/L *Mysidopsis bahia* (96-hr)		1644 (mg/L)	196.3 (72-hr)	>2000 (48-hr)	1.1	68.1[5]		Being used on East Coast of Canada

[1] Lethal concentration (LC_{50} in mg/kg dry weight of sediment unless otherwise stated)

[a] 10-d static toxicity test with the marine amphipod *Leptocheirus plumulosus*,

[b] 96-hr static toxicity test with the marine amphipod *Leptocheirus plumulosus*,

[c] 10-d static toxicity test with the sediment worker *Corophium volutor*,

[d] Toxicity test with the marine algae *Skeletonema costatum*, and

[e] Toxicity test with the marine copepods *Acartia tonsa*

[2] Bioaccumulation (Octanol-water partitioning coefficient)

[3] OECD 306 protocol for base fluid, conditions are untypical of cutting piles

[4] Protocol ISO/DIS 11734, conditions are similar to cutting piles

[5] OECD 301-B (after 28 days)

[6] Iso-alkane, Material Safety Data Sheet (Terra Nova, 2000)

Table 2.5. Material safety data sheet (MSDS) of synthetic based drilling fluids

(modified after Meinhold, 1998)

Base Fluid	Flash point (C)	Boiling point (C)	Vapor pressure (mm of Hg @ 20C)	Human health hazard
Esters	179	234[1]	≈ 0.066[1]	• Slight eye and skin irritation • Low acute inhalation toxicity • Ingestion causes irritation, nausea, vomiting and diarrhea
PAO	81	218-251	<0.1	• Repeated and prolonged exposures cause skin irritation and dermatitis
LAO	113	245-279	0.1	• Aspiration hazard • Causes drowsiness
IO	118	240	0.05 (at 40C)	• Aspiration hazard • Nuisance particulates • Repeated and prolonged exposures cause eye and skin irritation and dermatitis • Ingestion cause irritation, nausea, vomiting and cough
[2]IA	> 135	256-295	0.001	• Repeated and prolonged exposures cause eye and skin irritation • Repeated inhalation of excessive amount may cause irritation of respiratory tract • Oil deposits in lungs may cause fibrosis and pulmonary dysfunction

[1] Calculated by Quantitative Structure Activity Relationships (QSARs) (Lyman et al., 1990)

[2] Material Safety Data Sheet (Terra Nova, 2000)

The waste stream discharged from drilling operations that use SBFs or other non-aqueous drilling fluids consists of three main components: drilling fluid, drill cuttings, and formation oil. The U.S. EPA (1999a) has analyzed pollutant reduction options, compliance costs, and non-water quality environmental impacts, which are based on the drilling waste characteristics data given in Table 2.6. Formation oil is the only possible source of organic priority pollutants in the SBF cuttings waste stream. Formation oil contamination is an indicator pollutant of PAHs (U.S. EPA, 2000a). It includes naphthalene, fluorene, phenantherene and phenol. The estimated average adhering drilling fluid on the SBF-cuttings waste stream contains 0.2% formation oil by volume of SBF. Since the composition of formation (crude) oil varies widely, diesel oil is used to estimate the organic pollutant concentrations associated with formation oil (U.S. EPA, 2000a).

Table 2.6. Waste characteristics of SBF-cuttings

Priority Pollutant Organics		mg Pollutant/ml Formation Oil	
Naphthalene		1.43	
Fluorene		0.78	
Phenantherene		1.85	
Phenol		6.0	
Metals	mg/kg of Barite	Metals	mg/kg of Barite
Cadmium	1.1	Lead	35.1
Mercury	0.1	Nickel	13.5
Antimony	5.7	Selenium	1.1
Arsenic	7.1	Silver	0.7
Beryllium	0.7	Thallium	1.2
Chromium	240.0	Zinc	200.5
Copper	18.7		

Barite is used as a weighting agent and is the primary source of heavy metals in the drilling waste. The trace metal concentrations depend on the source of barite. The U.S. EPA and U.S. Department of Energy (U.S. DOE) have reported averaged trace metals concentrations based on data from more than 500 wells as shown in Table 2.6 (U.S. EPA, 1995, 2000a; Meinhold, 1998). Naturally occurring radioactive materials (NORM), such as potassium, strontium, uranium, thorium and radon can also be present in the formation oil, but are not reported by the U.S. EPA.

2.3. CONTAMINANTS FATE MODELING

Various processes, concepts and approaches have been used in determining the fate of drilling waste discharges in receiving water bodies. The present literature search indicates that no fully validated drilling waste discharge model exists which describes all the principles and processes in an appropriate framework. The transport and fate of drilling waste is a complex process, that is still only partially understood (Khondaker, 2000). Generally physical processes are employed in the fate modeling and other processes (and aspects) including chemical, biological and ecological are not incorporated. The transport of drilling waste involves (1) advection, (2) dispersion, (3) flocculation, (4) deposition, (5) consolidation, (6) erosion, and (7) resuspension. The impacts of these processes on the fate of drilling waste depend on the characteristics of the waste and the hydrodynamics of the receiving water bodies. The salient features and modular structure of such models are summarized in Figure 2.3. This structure is valid for those models, which consider only physical transport processes.

The other type of modeling approach is to consider the fate of contaminants based on their physico-chemical characteristics. The exposure concentrations of drilling waste chemicals using dilution factors and further partitioning of chemicals in the water column and sediments are estimated based on their bioaccumulation potential (K_{ow} and bioconcentration factors). These types of modeling approaches are popular in ecological risk assessment of wastes generated from offshore drilling operations. In the following sections a discussion of a few of the present state of the art modeling approaches is presented.

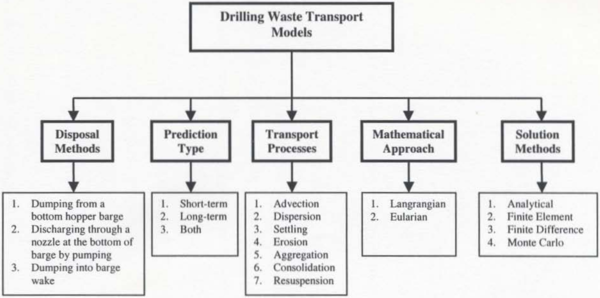


Figure 2.3. Important features of drilling waste transport models (modified after Khondaker, 2000)

2.3.1. U. S. EPA APPROACH

In the U.S. EPA study (1999a, b; 2000a, b), the SBF-cuttings discharge impact and water quality assessments rely on OOC (Offshore Operator's Committee) modeling data. Brandsma (1996) presented a model for the transport behavior of oil and solids from cuttings contaminated with oil-based fluids. Due to the similar hydrophobic (lower solubility in water) and physical properties (like vapor pressure and density) of SBFs and OBFs, the dispersion behavior of SBF-cuttings was assumed to be the same as those of OBF-cuttings (U.S. EPA, 1999a; Sadiq et al., 2000). In the water column, total organic pollutant discharge concentrations were assumed to represent the soluble concentration. Metals were assumed to leach or dissolve immediately into the water column with pollutant specific amounts determined for mean seawater pH.

Brandsma's study (1996) in the North Sea presented oil concentration as a function of transport time (Figure 2.4). Brandsma (1996) used 5.5% (by wet weight) oil content as the effluent to calculate the extent of dilutions available at various distances from the disposal location. Based on the mean OBF-cuttings density and the estimated initial oil concentration, available dilutions were determined at various distances from the disposal point. The water column pollutant concentrations at the edge of a mixing zone (at 100 m from the discharge) were calculated by dividing the drilling waste pollutant concentration by the dilution factor. The effluent concentrations for metals were further adjusted by a leaching factor (*LF*) to account for the portion of the total pollutant concentration that was dissolved and therefore available in the water column.

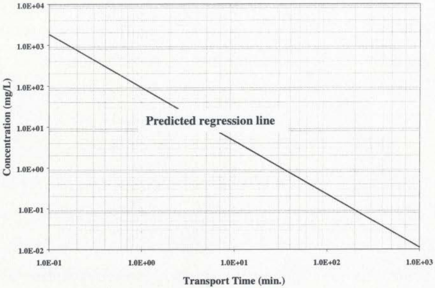


Figure 2.4. Oil concentrations as function of transport time (after Brandsma, 1996)

The US EPA (1999b) pore water quality analysis characterized sediment pollutants through a number of field surveys and the SBF itself was used as the marker for the pollutant presence due to its less dispersive behavior. In order to determine SBF-cuttings pollutant concentrations, it was assumed that the relative proportional concentrations between the base fluid and other pollutants were maintained after discharge and transport. The pollutant concentrations were converted into pore water concentrations using an equilibrium partitioning approach (EqP). For metals, the mean seawater leach factors of trace metals in barite were employed and for organic pollutants, partition coefficients were used to calculate the pore water concentrations. The partitioning coefficients estimate the ratio of sediment concentration to pore water concentration. The sediment concentration multiplied by the pollutant specific leach factor, or the inverse of the partitioning coefficient, gave the amount of pollutant available in the pore water. The analysis was conservative due to the assumption that discharged pollutants immediately leach into the water column or into pore water (interstitial water). Sadiq et al. (2000; 2001a, b) also used results of the OOC model for determining the fate of drilling waste for hypothetical case studies.

2.3.2. DEPOSITION MODELING

Seaconsult (2000) conducted a study for the Canadian offshore for the deposition modeling of synthetic base fluids attached to drill cuttings. The model predicts the SBF concentration (mg/kg of dry sediment) and thickness of cuttings on the seabed. The basic input for the model is the dry weight of discharged material. This model solves a regular Cartesian grid with a mesh size of 100 m. The model predicts the position of the contaminant based on the drill cutting size and density. The governing transport equation is solved using a particle-tracking technique. A set of discrete particles is released over time, and each particle and associated mass is defined. The procedure involves Monte Carlo (MC) simulations for simulating diffusive effects. The deposition model tracked the discharge of a single sediment class with a known characteristic grain size (δ in mm). The settling velocity (w) for particles more than 100 μm was defined by $4.2 \times \delta^{0.5}$, and for smaller size particles a constant value of 0.0012 m/s was assumed. The basic equations used for calculating base fluid concentration in the sediments and thickness of deposition on the seabed are given in Table 2.7.

The deposition model assumes that oil will remain attached to the cuttings during transport. The U.S. EPA (1999a) has made a similar assumption. This model determines the fate of SBF without considering the partitioning of base fluid within the multimedia. The resuspension, biodegradation, adsorption and other processes are not addressed in this model.

Table 2.7. Deposition model for determining synthetic oil concentration in the sediments (Seaconsult, 2000)

$$O_{j,k} = \frac{W_{j,k} \times 1000}{A} \tag{2.1}$$

where

j and k are x and y coordinates of the model cell/mesh, respectively.

$W_{j,k}$ = dry weight (kg) in cell j and k

A = Area of a cell (1 ha or 10,000 m^2)

$O_{j,k}$ = Deposition density or dry weight of sediment (g/m^2)

$$h_{j,k} = \frac{O_{j,k}}{\gamma} \tag{2.2}$$

where

γ = in situ bulk density (1850 kg/m^3)

$h_{j,k}$ = deposition thickness (mm) in cell j and k

$$C_{j,k} = \frac{C_{oil} \times W_{j,k}}{A \times h_m \times (1-n) \times \gamma_S} \tag{2.3}$$

where

γ_S = specific weight of mineral sediment (2600 kg/m^3)

n = seabed porosity (0.4)

h_m = sediment mixing depth (0.08m)

C_{oil} = initial oil loading (10^5 mg/kg)

$C_{j,k}$ = SBF concentration (mg/kg of dry sediment of sample)

2.3.3. bblt MODEL

Hannah et al. (1997) formulated and tested a basic bblt (benthic boundary layer transport) model. The key feature of the model is that it includes the process of vertical shear dispersion. The basic local bblt model assumes no horizontal variations in the ocean environment and allows continuous and bulk releases of sediment. The latest version, a "spatially-variable bblt" model, allows full spatial variability in water depth, currents, and bottom stress (boundary layer). These models partition the sediment load (drilling waste assumed on the seabed) into discrete pseudo-particles with mass m and velocity w_s. Shuffling of the packets represents vertical mixing which is defined by tidal currents. The bblt model output is the concentration profile throughout the depth based on the position of packet N. These models assume that drilling particles act as separate particles and are distributed based on particle size distribution. Another shortcoming of these models is that they do not consider the partitioning of contaminants within the water column and sediments.

2.3.4. PROTEUS (2001)

This model has been developed to simulate the dispersion of drilling waste discharges and subsequently disturbed cutting piles. Proteus (2001) considers the characteristics of discharged particulates and their size, and settling velocity during simulations. The settling velocities data from laboratory experiments have been used for the validation of algorithms used in Proteus to predict settling velocity. This model is used for water based drilling fluids in which desegregation of particulates after discharge happens.

This model simulates a 3-dimensional physical mixing process, which includes the initial dynamic discharge, the effects of density differences in the plume and surrounding fluid, and the transport by the current. This model also considers dynamic partitioning between particles and seawater, degradation and volatilization.

2.3.5. CHARM MODEL

The CHARM (Thatcher et al., 1999) model addresses only water based drilling chemicals. The PEC_{water} (Predicted Environmental Concentration) is calculated for continuous and batch discharges. The PEC_{water} values for both systems are calculated by simple mass balance equations by considering refreshment rate and dilution factors around the point of discharge. The refreshment rate is defined by dividing the residual current speed by the radius around the platform. Table 2.8 presents the summary of calculations for determining concentrations in the water column and sediments. The $PEC_{sediment}$ is defined by using the water-sediment partitioning coefficient (K_{sw}). $PEC_{sediment}$ is further adjusted by biodegradation, which is arbitrarily selected for one-year time to reduce the predicted environmental concentration. The CHARM model uses a simplified approach for calculating exposure concentrations and does not address the fate of SBFs and OBFs in the marine system.

2.3.6. MASS TRANSPORT MODEL

Thibodeaux et al. (1986) have developed a mass transport model for the chemical contaminants originating from offshore drilling deposits. This model was limited to the transport of the soluble constituents of the cuttings and mud deposits. This model did not take into account particulate transport and chemical and biochemical transformations that degrade contaminants within the sediment zone or boundary layer.

Table 2.8. Concentration calculations for CHARM model
(modified after Thatcher et al., 1999)

Dosage expressed as weight percentage

$$M = Wt \times V_m \times \rho_m \tag{2.4}$$

where

M = *amount (mass) of pollutant discharged (kg)*
Wt = *weight percentage of the pollutant in the mud*
V_m = *volume of mud discharged for the specific section (m^3)*
ρ_m = *density of the discharged mud (kg/m^3)*

Volume of ambient water available for dilution

$$V_p = \frac{1}{platform\ density} \times waterdepth \times 10^6 \tag{2.5}$$

where

V_p = *volume of ambient water per platform (m^3)*
Plat form density = *number of platforms per square kilometre (1/km)*
Water depth = *average water depth around the platform (m)*

Refreshment rate of the ambient water

$$r = \frac{24 \times 3600}{2 \times Y/U} \tag{2.6}$$

where

r = *fraction of sea water refreshed in the area around the platform (1/day)*
Y = *radius around platform (m)*
U = *residual current speed (m/s)*

The volume of water passing the platform during the period of drilling a section

$$V_t = V_p \times r \tag{2.7}$$

where

V_t = *volume of water passing the platform (m^3/d)*
V_p = *volume of ambient water per platform (m^3)*
r = fraction of sea water refreshed in the area around the platform *(1/day)*

PEC_{water} for continuous discharges can now be calculated using

$$PEC_{water,cont} = \frac{M}{T \times V_t} \times 10^3 \tag{2.8}$$

where

$PEC_{water,cont}$ = *PEC_{water} for continuous discharges (mg/L)*
M = *amount (mass) of pollutant discharged (kg)*
T = *time needed to drill a section (d)*
V_t = *volume of water passing the platform (m^3/d)*

$$PEC_{sediment} = PEC_{water,cont} \times K_{sw} \times (1 - d_{s365}) \tag{2.9}$$

where

$PEC_{sediment}$ = *PEC in the sediment around the platform (mg/kg)*
$PEC_{water,cont}$ = *PEC_{water} for continuous discharges (mg/L)*
K_{sw} = *sediment-water partition coefficient (L/kg)*
d_{s365} = *fraction of a substance in sediment that is degraded in one year*

2.3.7. FUGACITY BASED MODELS

Environmental thermodynamics generally applies to a narrow temperature range between 0° to 25C° and the pressures are generally atmospheric except for additional hydrostatic pressures underwater. These special conditions in environmental fate modeling help in simplifying the complex thermodynamic models dealing with the fate of contaminants (Mackay. 1991). Generally two approaches are used to develop equations relating equilibrium concentrations in two phases. The most common approach is Nernest's Distribution Law. which states that the concentration ratio (C_1/C_2) is relatively constant and equal to partition/distribution coefficient K_{12}. Linear and non-linear equations can be fitted to the data to calculate the rate constants. The second approach needs an intermediate parameter. a criterion of equilibrium. which can be related to C_1 and C_2. separately. Chemical potential. fugacity. and activity are common parameters. Fugacity is the most common criterion for organic substances (Mackay. 1991).

In the environment. chemicals migrate from one phase to another. The fraction of a compound between the different phases at equilibrium is determined by minimization of Gibbs's free energy (*G*) (Moran and Shapiro. 1988). *G* is a function of enthalpy (*h*) and entropy (*S*).

$$\frac{G}{n} = g = h - TS \tag{2.10}$$

where

G = Gibbs's free energy (Joules)

h = Enthalpy (Joules/mole)

T = Temperature (K°)

S =Entropy (Joule/mole·K°)

n = Number of moles

g = Gibbs's free energy/mole (Joules/mole)

In differential form above equation reduces to

$$dg = dh - d(TS) \tag{2.11}$$

where

$$dh = v\,dP + T\,dS \tag{2.12}$$

and

$$d(TS) = T\,dS + S\,dT \tag{2.13}$$

Therefore equation 2.11 becomes

$$dg = (v\,dP + T\,dS) - (T\,dS + S\,dT) \tag{2.14}$$

$$dg = v\,dP - S\,dT \tag{2.15}$$

For an ideal gas

$$P\,v = RT \tag{2.16}$$

where

v = Volume per unit mole (V/n), and
R = Universal gas constant

Therefore equation 2.15 becomes

$$dg = \frac{RT}{P}dP - S\,dT \tag{2.17}$$

If temperature (T) is constant

$$dg = RT\,d(\,LnP\,)_T \tag{2.18}$$

The ideal gas behavior is applicable over a limited range of pressure and temperature, therefore to account for non-ideal behavior a property called fugacity (f) is introduced. Therefore equation 2.18 becomes

$$dg = RT\,d(\,Ln\,f\,) \tag{2.19}$$

Fugacity has units of pressure and reduces to pressure as ideal gas conditions are approached (i.e., pressure $P \rightarrow 0$).

$$\lim_{P \to 0} \frac{f}{P} = 1 \tag{2.20}$$

Therefore final relation becomes

$$RT\, d(\, Ln\, f\,) = v(\, d\, P\,)_T \tag{2.21}$$

Fugacity may now be determined by using equations for pressure or volume, which account for non-ideal behavior. Therefore the molar concentration and fugacity relationship can be defined from an ideal gas law.

$$C = \frac{n}{V} = \frac{P}{RT} = \frac{f}{RT} = Zf \tag{2.22}$$

where Z is the fugacity capacity and establishes values for each chemical in each phase. This process starts from the air phase (Z_A) in which it can be shown that

$$Z_A = \frac{1}{RT} \tag{2.23}$$

If an air-water partition coefficient K_{AW} is available, the value of Z for a chemical in water can be calculated by taking f_A (air fugacity) equal to f_W (water fugacity).

$$C_W = {}^{C_A}\!\big/_{K_{AW}} \quad \therefore \text{ Generally, } C_2 = C_1 K_{21} \tag{2.24}$$

It is thus possible to calculate Z_i values for chemicals in soil, fish, and sediments if the partitioning coefficients are known. The relationships have been developed for partitioning coefficients of several organic chemicals as a function of chemical properties, such as solubility in water, K_{ow} and vapor pressure. The expressions of these relationships are given in Table 2.9.

Table 2.9. Definition of fugacity capacities (*Z*)

Compartment	Definition of Z (mol/m^3-Pa)
Air	$1/RT$ R = 8.314 mol/m^3 Pa and T = Temperature (K)
Water	$1/H$ or C^S/P^S C^S = Aqueous solubility (mol/m^3) P^S = Vapor pressure (Pa) H = Henry's law constant (Pa. m^3/mol)
Solid sorbent (e.g. soil, sediment and particles)	$K_P \rho_S / H$ K_P = Partition coefficient (L/kg) ρ_S = Density (kg/L)
Biota (fish)	$K_B \rho_B / H$ K_B = Bioconcentration factor (L/kg) ρ_B = Density (kg/L)

Fugacity concepts have been successfully applied in pharmacokinetics, food uptake of plants, sewage treatment plants, and regional distribution of pollutants (Mackay, 1991; Mackay et al., 1992; Mackay and Paterson, 1990). The fugacity approach is convenient for complex ecological systems and has been extensively used in modeling the distribution of contaminants in multimedia environments. The use of fugacity instead of concentration defines the equilibrium status of phases and the direction of diffusive transfer.

Mackay (1991) developed a methodology for estimating chemical distributions in multimedia based on the level of complexity of the systems, namely

Level I: Equilibrium, Steady state, and No-flow system,
Level II: Equilibrium, Steady state, and Flow system,
Level III: Non-equilibrium, Steady state, and Flow system and
Level IV: Non-equilibrium, Unsteady state, and Flow system.

In Level I, the equilibrium partitioning of a fixed amount of non-reacting compound is calculated using fugacity capacities that are derived from physico-chemical data. The equilibrium ratios of concentrations and the relative amounts in each phase can be calculated. In Level II, the steady state equilibrium concentrations are calculated for fixed emissions that are balanced by reactions of various types in each phase. This provides the information on the compound's overall persistence and about the proportion that reacts in each phase. The critical limitations of Levels I and II are the assumptions of achieving equilibrium between all phases. In practice, there is a transfer resistance that limits the transfer from one phase to another and then tends to contain the chemical within that phase. Interphase transport resistance defines Level III in which each phase may have a different fugacity. Level IV introduces the concept of inflows (emissions) that change with time, i.e. non-equilibrium and unsteady state condition. If emissions are constant, the Level IV will approach Level III (Mackay, 1991).

2.4. POTENTIAL FUGACITY/AQUIVALENCE BASED APPROACH

A level III version of the fugacity model called the QWASI model was developed by Mackay et al. (1983) and applied to rivers and lakes, specifically for detergent chemicals, PCBs and heavy metals. In the QWASI model, the steady state solution describes conditions that will be reached after prolonged exposure of the system to constant input conditions. The use of fugacity as an equilibrium criterion is suitable for chemicals that can establish measurable concentrations in the vapor phase. It is not applicable to some metals, organometals, ionic compounds, nor some organics such as polymers whose vapor pressure is negligible. To model the behavior of these chemicals, another equilibrium criterion analogous to fugacity is used. This criterion is known as the aqueous equivalent concentration (aquivalence) criterion, which is suitable for both volatile and non volatile chemicals (Mackay and Diamond, 1989). A model developed in terms of aquivalence is ultimately similar to models written in terms of concentration or fugacity. The aquivalence model has been applied to the multi-phase distribution of inorganic chemicals assuming they behave as single species, such as total lead. The fugacity/aquivalence approach has been extensively applied to Lake Ontario and Hamilton Harbor for various heavy metals and organic chemicals (Mackay and Diamond, 1989). The QWASI model takes into account advective flow, volatilization, sediment deposition, resuspension, and burial, sediment-water diffusion, and transformation reaction processes (Mackay et al., 1983).

In levels higher than Level I, the rates of loss through reaction and advection are considered. The degradation rates for chemicals are defined by a first order rate constant (k) or calculated from a half-life ($H_{1/2}$) in each medium. The transformation and transportation processes are calculated in terms of D-values. The rate constant k (hr^{-1}) is used to calculate a reaction D-value D_R in each medium. The D_R is defined as

$$D_R = V_i \times Z_i \times k_i \tag{2.25}$$

where

V_i = Volume (m^3)

Z_i = Fugacity capacity ($\mathrm{mol/m^3\text{-}Pa}$)

k_i = Reaction rate constant (hr^{-1})

$i = i^{th}$ medium

The rate of reactive loss (E_R, mol/hr) is calculated by multiplying D_R with fugacity, f. Similarly, for calculating advection losses, flow rates (Gi), or detention times are defined. The D-value for advection (D_A) is defined as $Gi \times Zi$ and the advection rate of loss (E_A, mol/hr) as the product of D_A and f.

At Level III additional diffusive and non-diffusive processes of intermedia transport are taken into account. In conventional 4 media systems, Mackay and co-workers have defined 12 intermedia transport velocity parameters (U_1 to U_{12}). These parameters are used to calculate the intermedia transport *D*-values. Mackay (1991) defined four primary compartments namely, air, water, soil and sediments. The air is defined as a mixture of aerosols; water as mixture of suspended particles and fish; soil as solids, water and air; and sediments as solids and pore-water. Different media are assigned the following numerals:

Media	Numeral
Air	1
Water	2
Soil	3
Sediment	4
Suspended solids	5
Fish	6

Air and soil compartments are not relevant to the present research, which will deal mainly with two primary compartments, i.e., water and sediments. The intermedia mass transport means water-to-sediment diffusion and advection through interface and vice versa. Different mechanisms of transport and transformation in the two-compartment model are shown in Figure 2.5. Intermedia transport velocities U_8, U_9 and U_{10} represent sediment-water mass transfer through diffusion, sediment deposition and sediment resuspension, respectively. The intermedia *D*-values for water to sediment (D_{24}) and sediment to water (D_{42}) are calculated by relations given in Table 2.10. D_{24} accounts for mass transfer from water to sediment and deposition of suspended solids. Similarly D_{42} accounts for mass transfer from sediment to water and resuspension of sediments to the water column. The kinetics of resuspension and deposition of suspended solids (*SS*) are discussed in the next chapter using Huang's (1992) experimental results.

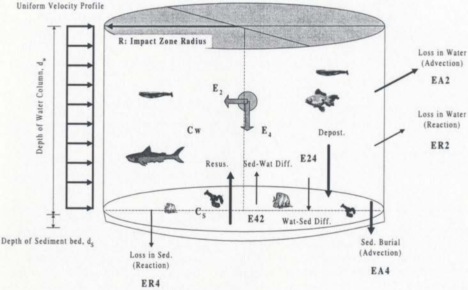


Figure 2.5. Water sediment interaction model

The advection and reaction *D*-values in water and sediments are calculated based on flow rate and half-life of pollutants. First order kinetics is applied to determine the reaction rate constant and *D*-values (D_{R2} and D_{R4}). Similarly, knowing the burial rate of sediments and the detention time in the water column, D_{A2} and D_{A4} can be calculated, respectively. The calculations of fugacity (*f*) are based on Mackay et al.'s (1992) work, but have been modified to suit a two-compartment system of water and sediment. A systematic procedure for calculating the concentration in water and sediment is summarized in Table 2.10.

Table 2.10. Procedure for calculating concentrations in water column and pore water

No.	Comments and instructions	Parameters and Equations
1	Define physico-chemical properties of pollutant.	Henry's coefficient (H), solubility (S), K_{ow}, etc.
2	Define media (sediment and water) physical properties.	Volume (V) and surface area (A_W), depths of water column (d_w) and sediment (Δ), volume fractions (v), densities (ρ) etc.
3	Define flow rates or advection velocities in water-sediment system. Similarly reaction rates can be determine from half lives ($H_{1/2}$) or kinetic coefficients (k) in water and sediments.	G_i (flow rate) = volume/detention time $k = 0.693/H_{1/2}$ for first order kinetics
4	Calculate the fugacity capacity (Z) of all components. ϕ =organic fraction ρ = density K_{OC} = Portioning coefficient for organic carbon content	$Z_2 = 1/H$ (H: Henry's coefficient) $Z_4 = Z_2\, \rho_4\, \phi_4\, K_{oc}$ $Z_5 = Z_2\, \rho_5\, \phi_5\, K_{oc}$ $Log(K_{oc}) = 0.544 \times Log(K_{ow}) + 1.377$ $Z_6 = Z_2\, \rho_6\, \phi_6\, K_{oc}$ ⇧ Using QSAR as given in Lyman et al. (1990).
5	Calculate the bulk Z values (Z_B) for primary compartments, i.e., water and sediment v = volume fraction	$Z_{B2} = Z_2 + v_5 Z_5 + v_6 Z_6$ *and* $Z_{B4} = Z_2 \times (pore\ water) + Z_4 \times (solid\ particles)$
6	Calculate process D-values (mol/Pa·hr) Reaction Advection	$D_{R2} = Z_{B2}\, V_2\, k_2$ *and* $D_{R4} = Z_{B4}\, V_4\, k_4$ $D_{A2} = Z_{B2}\, G_2$ *and* $D_{A4} = Z_{B4}\, G_4$
7	Define pollutant loads by direct emissions in water (E_2) and sediments (E_4)	
8	Calculate intermedia transport D-values Where Z_2, Z_4, Z_5 are fugacity capacities of water, sediment and suspended solids, respectively, and A_W is the area of water-sediment interface.	$D_{24} = A_W U_8 Z_2 + A_W U_9 Z_5$ $D_{42} = A_W U_8 Z_2 + A_W U_{10} Z_4$ U_8 = sediment-water mass transfer coefficient (MT) U_9 = SS deposition } Based on Huang (1992) U_{10} = sediment resuspension } and Seaconsult (2000)
9	Calculate total D-values	Water $D_{T2} = D_{R2} + D_{A2} + D_{24}$ Sediment $D_{T4} = D_{R4} + D_{A4} + D_{42}$
10	Making mass balance equations under steady state conditions Water: $E_2 + f_4 D_{42} = f_2 D_{T2}$ *and* ⇨ Sediment: $E_4 + f_2 D_{24} = f_4 D_{T4}$ Now solve for fugacities (f_i)	$f_2 = \dfrac{E_2 + \dfrac{E_4 D_{42}}{D_{T4}}}{D_{T2} - \dfrac{D_{24} D_{42}}{D_{T4}}}$ *and* $f_4 = \dfrac{(E_4 + f_2 D_{24})}{(D_{T4})}$
11	Calculate concentrations (mg/L) MW = Molecular weight	$C_W = MW \times Z_2 \times f_2$ (*water column*) $C_{PW} = MW \times Z_2 \times f_4$ (*pore water*) $C_{BW} = MW \times Z_{B2} \times f_2$ (*bulk water column*) $C_{BS} = MW \times Z_{B4} \times f_4$ (*bulk sediments*)
12	Calculate the emissions through each process in different media	$E_{R2} = D_{R2} f_2$ $E_{R4} = D_{R4} f_4$ $E_{A2} = D_{A2} f_2$ $E_{A4} = D_{A4} f_4$ $E_{T2} = D_{R2} f_2 + D_{A2} f_2$ $E_{T4} = D_{R4} f_4 + D_{A4} f_4$
13	Check total emissions (E) Calculate total mass (M) Calculate overall residence time (t_O)	$E = E_2 + E_4$ *and* $M = \Sigma\, [C \times V]$ *and* $t_O = M/E$

As mentioned earlier, the use of fugacity as an equilibrium criterion is suitable only for chemicals that can establish measurable concentrations in the vapor phase, but is not applicable to metals, organometals, nor ionic compounds that have negligible or zero vapor pressure. For these types of chemicals an alternative equilibrium criterion, "aquivalent concentration" or "aquivalence" *(A)* is recommended (Mackay and Diamond, 1989). The *(A)* criterion has the dimensions of concentration but the Z' values become dimensionless. The simpler way to look at this criterion is the "equivalent equilibrium aqueous phase" concentration, and so the dimensionless Z_2' value becomes equal to 1. In case of the water phase, *(A)* is the actual concentration. The Z' for other phases becomes the dimensionless partition coefficients, e.g.

$$\left.\begin{aligned} Z_2' &= 1 \\ Z_4' &= \rho_4 K_\sigma \\ Z_5' &= \rho_5 K_\pi \\ Z_6' &= \rho_6 K_B \end{aligned}\right\} \qquad (2.26)$$

where K_σ, K_π and K_B are the partitioning coefficients for sediment, particulate matter and bioconcentration factor for biota, respectively. The procedure of calculating concentrations as described in Table 2.10 will remain the same but parameters of Z and f will be replaced by Z' and A, respectively.

This chapter has discussed main research issues: firstly, various types of drilling fluids and their characteristics were discussed from ecological and human health risk viewpoints: secondly, various state of the art modeling approaches used in determining the fate of drilling waste in the marine environment were discussed. In the end, a step by step methodology was presented for a proposed water-sediment interaction model that will be used in the next chapter for applying a probabilistic approach for determining the fate of drilling waste.

Chapter 3

METHODOLOGY FOR PROBABILISTIC FATE MODELING

This chapter deals with various steps involved in the development of a methodology for fate modeling. Drilling waste is a mixture of various types of pollutants. The physico-chemical characteristics of the pollutants and the multimedia environment in which they disperse, govern the ultimate fate of the pollutants. The variability and uncertainty in input variables and the model's structure determine the uncertainty in the model's outputs. A parametric based probabilistic approach is adopted for a fugacity/aquivalence based water sediment interaction model in which the model inputs are defined by statistical distributions.

Monte Carlo (MC) simulations using Latin Hypercube Sampling (LHS) were performed to determine the model outputs: water column concentration (C_w), pore water concentration (C_{PW}), and their associated uncertainties. The sensitivity analysis (SA) was performed using the rank correlation coefficient (ρ_c) and by estimating the percent contribution of input variables to the variance of the model's output. The key input variables of the water sediment interaction model were identified. In the end, multiple linear regression models were developed to predict environmental concentration in multimedia as a function of pollutant loading rate (*E*) and radius of impacted area (*R*). A chemical specific approach was employed in the fate modeling. The pollutants under consideration were arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb), zinc (Zn), base fluid (ester), and naphthalene.

In adopting a parametric probabilistic approach using MC simulations for fate modeling, a four-step process was followed. In the first step, a detailed literature search was conducted to determine the values and/or ranges of various inputs to the model, which included physico-chemical characteristics of the pollutants and multimedia properties. The statistical distributions of model inputs were selected subjectively in the second step. Then in the next step, MC simulations were performed to estimate concentrations in the water column and pore water and their associated uncertainties. The key input variables were identified using sensitivity studies in MC simulations results. Finally, empirical regression models were developed to determine the representative environmental concentration of the pollutants in terms of the pollutant loading rates and impact area. This four-step fate modeling process is shown in Figure 3.1. The details of these steps are discussed in the following sections.

3.1. PARAMETER SELECTION

The quantities of drill cuttings produced are proportional to the rate of advancement of a drill bit downhole. The U.S. EPA (2000a) estimated the pollutant weights and volumes in the drilling waste streams for various types of model wells from the data provided by the American Petroleum Institute (API). The drill cuttings are brought to the surface and drilling fluids are separated from the cuttings by a solid separation system that may include shale shakers and centrifuges. The drilling fluid is reused provided its rheological characteristics meet the technical requirements of drilling. The drill cuttings, which also carry residual drilling fluid, are typically discharged continuously during drilling operations (Meinhold, 1998).

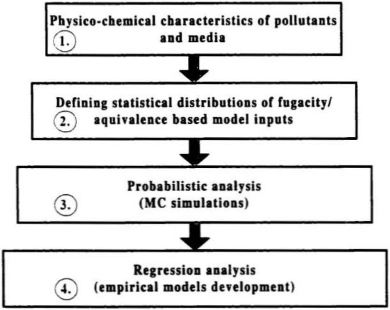


Figure 3.1. A four-step process of fate modeling methodology

The drill cuttings and the attached drilling fluid are high-density suspended solids, which may cause benthic smothering and sediment grain size alteration upon discharge in the marine environment. In addition to the physical impacts of drilling wastes, the SBFs are comprised of conventional and non-conventional pollutants, which may be toxic in nature and have bioaccumulation potential. The drilling waste may cause hypoxia (reduction in oxygen) in the immediate sediments depending on bottom currents, temperature and rate of biodegradation.

Barite has a specific gravity of 4.6 and is used as a weighting agent in drilling fluid. It accounts for approximately 33% of total SBF weight. Barite consists mainly of barium sulphate, but also contains traces of heavy metals, which include arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn). Generally the trace heavy metals present in barite are reported in terms of mg/kg of barite (U.S. EPA, 1999b). The sole source of poly aromatic hydrocarbon (PAH) in the synthetic based drilling waste stream is contamination by formation oil. On average, the formation oil is 0.2% (by volume) of SBFs. Due to the variable composition of formation oils, diesel oil is recommended for estimation of quantities of organic pollutants (U. S. EPA, 2000b).

The following sections will deal with specific physico-chemical characteristics of fugacity/aquivalence-based water sediment interaction model inputs, which are pollutants and media properties.

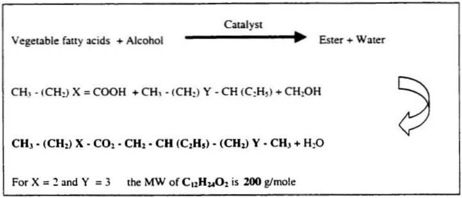
3.1.1. PHYSICO-CHEMICAL PROPERTIES OF THE POLLUTANTS

The whole toxicity and the chemical specific approaches are generally employed for fate modeling and exposure assessment in the risk assessment framework. In the chemical specific approach, each pollutant present in the waste is treated individually based on its own physico-chemical characteristics. A similar approach is employed by the U.S. EPA (2000a) and in the CHARM model (Thatcher et al., 1999) for drilling wastes fate modeling. The drilling waste as a single entity can be considered in the fate model provided that the physico-chemical characteristics are known. In the absence of the substantial data required for fate modeling, the whole toxicity approach is not possible to implement. Therefore the chemical specific approach was employed in this research.

The behaviour and fate of a pollutant in the environment depends on its physico-chemical characteristics. The major characteristics include Henry's coefficient (H), bioaccumulation potential (K_{ow}), heavy metals partitioning coefficients for sediments (K_{σ}) and suspended solids and particulates (K_{τ}), half lives in water and sediment ($H_{1/2}$ and $H_{1/2\sigma}$), and mass transfer coefficient (MT *or* U_s). Table 3.1 summarises these physico-chemical characteristics of pollutants.

Mackay and co-workers (e.g., Mackay et al., 1992) have recommended a fugacity based approach for those organic compounds that can maintain vapour pressure in air. For ester and naphthalene a fugacity-based approach will be used in a water sediment interaction model. The base fluid (ester) present in SBF is considered to be one of the pollutants in a drilling wastestream. Ester is used here as the base fluid, as it is the most popular base fluid among the synthetic based fluid family. Esters are obtained by crushing palm oil kernels. The oil is split into fatty acids and glycerol, which after fractionation is mixed with 2-ethyl hexanol in the presence of a catalyst to give a vegetable ester. Generally 8 to

12 carbon atoms are present in the ester molecules. A general formulation of an ester molecule is given in Figure 3.2 (Hall, 2000). The molecular weight (MW) for ester is 200, based on the molecular formula given in Figure 3.2.



Vegetable fatty acids + Alcohol $\xrightarrow{\text{Catalyst}}$ Ester + Water

$CH_3 - (CH_2) X = COOH + CH_3 - (CH_2) Y - CH (C_2H_5) + CH_2OH$

$\mathbf{CH_3 - (CH_2) X - CO_2 - CH_2 - CH (C_2H_5) - (CH_2) Y - CH_3} + H_2O$

For $X = 2$ and $Y = 3$ the MW of $\mathbf{C_{12}H_{24}O_2}$ is **200** g/mole

Figure 3.2. Synthesis of esters from fatty acids (palm oil) and alcohol

Henry's coefficient (*H*) is the most important parameter for organic pollutants in the fugacity based models. It is used to estimate the fugacity capacity in water (Z_2). The *H* provides a relationship for pollutant concentration in air and water. The *H* is the ratio of vapour pressure (*P*) and pollutant solubility in water (*S*). The experimental *H* value for ester is not reported in the literature. In the absence of experimental values, the QSARs (Quantitative Structure Activity Relationship) are used to determine an *H* value (Lyman et al., 1990). The quantitative structure activity relationships are based on laboratory data that correlate different physico-chemical characteristics of the pollutant. The QSAR for solubility and values of vapour pressure are used to estimate the *H* for ester (Lyman et al., 1990). The estimated value of H is in the range of 0.10 to 0.15 m^3·Pa/mol (Table 3.1). The H values for naphthalene are extensively reported in the literature. The reported experimental values for H are in the range from 42 to 56 m^3·Pa/mol (Howard, 1989; Diamond et al., 1994). The H is not relevant parameter for heavy metals and an aquivalence based approach is used.

The mass transfer through diffusion is estimated with the help of a diffusion coefficient (D_{BW}). It is also calculated using QSAR because experimental values are not reported. The molecular formula of ester is used to estimate the diffusion coefficient (0.19×10^{-5} m^2/hr) (Lyman et al., 1990). The mass transfer coefficient (MT *or* U_s) can be calculated by dividing D_{BW} with the path length or sediment mixing depth (Δ). Seaconsult (2000) used an 8 cm sediment mixing depth to determine oil concentration on the seabed. Brandsma (1996) proposed a 4 to 9 cm thick sediment layer. For this range of thickness, the estimated MT for ester may vary from $(2 \text{ to } 5) \times 10^{-5}$ m/hr. For naphthalene and heavy metals, MT values are reported in the range of $(1 \text{ to } 4) \times 10^{-4}$ m/hr (Table 3.1).

The bioaccumulation potential of an organic compound is determined by the partitioning coefficients for organic carbon (K_{OC}). It is used to estimate fugacity capacity in sediment (Z_4) and suspended solids (Z_5). The log of the octanol-water partitioning coefficient (K_{OW}) is reported to be 1.69 (U.S. EPA, 1999b; Hall, 2000). The K_{OC} values are related to K_{OW} by a QSAR as given in Table 3.1 (Lyman et al., 1990). The log of octanol-water partitioning coefficient (K_{OW}) for naphthalene is reported to be 3.30 (U.S. EPA, 1999a) but Howard (1989) has also reported experimental values of K_{OC} in the range of 400 to 1000.

Table 3.1. Physico-chemical properties of selected pollutants in drilling waste stream

Pollutant	Approach	*MW/AW*	Henry's Coefficient (*H*) m^3 pa/mol	K_{ow} or K_p & K_d L/kg	$H_{1/2o}$ days	$H_{1/2}$ days	*MT* or U_B m/hr
Esters $C_{12}H_{24}O_2$	Fugacity	$^{a}200$	$^{b}\mathrm{Log}(1/S) = 1.013 \times \mathrm{Log}(K_{ow}) - 0.52$ $S = 64$ mol/m^3 $P = 8 - 9$ Pa $H = 0.1 - 0.15$	$^{a,c}\mathrm{Log}K_{ow} = 1.69$ $^{b}\mathrm{Log}(K_{oc}) = 0.544 \times \mathrm{Log}(K_{ow}) + 1.377$ K_{oc} = organic carbon partitioning coefficient	$^{c}16$ to 22	$^{c}12$ to 130	$^{b}D_{BW} = 0.191 \times 10^{-5}$ m^2/hr $^{k,l}\Delta = 4 - 9$ cm $U_B = D_{BW}/\Delta$ $U_B = (2 - 5) \times 10^{-5}$ m/hr
Naphthalene		128.2	$^{c}49\text{-}56$ $^{d}42.1$	$^{c}K_{ow} = 1995$ $^{c,j}K_{oc} = 0.41 \times K_{ow}$ and $^{c}400$ to 1000	$^{c}25$ to 258	$^{c}0.5$ to 20	
Lead (Pb)	Aquivalence	207.2	$^{g,h}K_p = 6.68 \times 10^5$ (*SS*/water) $^{g,h}K_d = 3.33 \times 10^5$ (sediment/water)	; $^{m}(\mathrm{Log}K_p$ range $= 3.4 - 6.5)$; $^{m}(\mathrm{Log}K_d$ range $= 2.0 - 7.0)$	$^{g,h}1 \times 10^{20}$	$^{g,h}1 \times 10^{20}$	
Mercury (Hg)		272	$^{i}K_p = 0.5 - 2 \times 10^5$ $^{i}K_d = 0.5 - 2 \times 10^4$	; $^{m}(\mathrm{Log}K_p$ range $= 4.2 - 6.9)$; $^{m}(\mathrm{Log}K_d$ range $= 3.8 - 6.0)$	$^{i}25 - 2000$	$^{i}64$ years	
Arsenic (As)		74.9	$^{d}K_p = 1.0 \times 10^4$ $^{j}K_d = 1.3 \times 10^4$	; $^{m}(\mathrm{Log}K_p$ range $= 2.0 - 6.0)$; $^{m}(\mathrm{Log}K_d$ range $= 1.6 - 4.3)$	$^{d}-$	$^{d}-$	$^{l}U_B = 1.0 \times 10^{-4}$
Copper (Cu)		63.6	$^{d}K_p = 2.0 \times 10^4$	; $^{m}(\mathrm{Log}K_p$ range $= 3.1 - 6.1)$ $^{m}(\mathrm{Log}K_d$ range $= 0.7 - 6.2)$	$^{d}-$	$^{d}-$	$^{l}U_B = 2.0 \times 10^{-4}$
Chromium (Cr)		52.0		$^{m}(\mathrm{Log}K_p$ range $= 3.9 - 6.0)$ $^{m}(\mathrm{Log}K_d$ range $= 1.9 - 5.9)$			$^{g,h}U_B = 4.0 \times 10^{-4}$
Zinc (Zn)		65.4	$^{g}K_p = 1.0 \times 10^5$ $^{g}K_d = 5.2 \times 10^4$	; $^{m}(\mathrm{Log}K_p$ range $= 3.5 - 6.9)$; $^{m}(\mathrm{Log}K_d$ range $= 1.5 - 6.2)$	$^{g}1 \times 10^{20}$	$^{g}1 \times 10^{20}$	
Nickel (Ni)		58.7		$^{m}(\mathrm{Log}K_p$ range $= 3.5 - 5.7)$ $^{m}(\mathrm{Log}K_d$ range $= 0.3 - 4.0)$			
Cadmium (Cd)		112.4	$^{d}K_p = 3.2 \times 10^5$	; $^{m}(\mathrm{Log}K_p$ range $= 2.8 - 6.3)$ $^{m}(\mathrm{Log}K_d$ range $= 0.5 - 7.3)$	$^{d}-$	$^{d}-$	

a Hall (2000)
b Lyman et al. (1990)
c Howard (1989)
d Diamond et al. (1994)
e U.S. EPA (1999b)
f Mackay et al (1992)

g Ling et al. (1993)
h Mackay and Diamond (1989)
i Diamond (1999)
j Stansbury (1991)
k Brandsma (1996)
l Seaconsult (2000)
m U.S. EPA (1999c)

The reaction rate coefficient (k) determines the biodegradation potential of organic pollutants. It can be determined by half-lives of organic pollutants using first order kinetics. The organic pollutants degrade at different rates in water and sediments. Based on aqueous and sediment phase anaerobic biodegradation tests, the range of ester half-lives in water ($H_{1/2}$) and sediments ($H_{1/2\sigma}$) are reported to be 16 to 22 days and 12 to 130 days, respectively (Table 3.1). The details of experimental results are summarised by the U.S. EPA (1999b). The half-lives of naphthalene in sediment ($H_{1/2\sigma}$) and water ($H_{1/2}$) under anaerobic conditions may range from 25 to 258 days and 0.5 to 20 days, respectively (Howard, 1989). Heavy metals are not biodegradable and the half-lives of 1×10^{20} years or more are generally assumed in the aquivalence-based fate modeling (e.g., Ling et al., 1993).

In the aquivalence based approach, the aquivalence capacity (Z') is determined using the partitioning coefficient from water to *SS* (K_{τ}) and water to sediment (K_{σ}). The values of partitioning coefficients may vary with a change in hardness and pH. Some equilibrium speciation computer models including, *MINEQL+* and *MINTEQA2* are also used to estimate the equilibrium partitioning of the metals (U.S. EPA, 1999c). Diamond et al. (1994), Diamond (1999) and Ling et al. (1993) have reported the partitioning coefficient values for various heavy metals. The U.S. EPA (1999c) has summarised the data for a range of partitioning values in various media including soil/water, sediment/water and *SS*/water. The range of K_{τ} and K_{σ} values are summarised in Table 3.1.

3.1.2. MEDIA CHARACTERISTICS

The next step in the fate modeling is to define the physico-chemical nature of the environment in which pollutants are discharged. The marine environment consists of two basic compartments: sediment and water. The sediment layer consists of water and solid particles and the water column contains *SS* and biota. The media (water and sediments) characteristic parameters include density (ρ), volume fraction (v), organic content (ϕ) and various coefficients used in determining the deposition of *SS*, resuspension and burial rates of sediments. Table 3.2 summarises the media characteristic values.

The layer of sediments just above the seabed is very loose and contains high water content. The volume fraction (v_4) of the pore water in sediments may range as high as 0.7 to 0.92 in the lake system (Mackay and co-workers). Seaconsult (2000) and Brandsma (1996) used a volume fraction of 0.4 in drilling waste fate modeling, which represents medium to coarse mixed sand porosity. Sleath (1984) has suggested a range of 0.35 to 0.5 (mixed sand to silt) for the seabed. Similarly, the *SS* volume fraction (v_5) is reported in the range of 0.2 to 50 ppmv (parts per million by volume) (Mackay and co-workers). The Terra Nova (1996) Environmental Impact Assessment (EIA) reported v_5 in the range of 10 to 2770 ppmv on the Grand Banks.

The densities of *SS* (ρ_5) and dry sediments (ρ_4) are reported in the range of 1500 to 2400 kg/m^3 and 2000 to 2640 kg/m^3, respectively (Mackay and co-workers). Seaconsult (2000) has reported insitu bulk density (ρ_5) of 1850 kg/m^3 and specific weight of mineral sediment (ρ_4) of 2596 kg/m^3 for the Georges Bank. Brandsma (1996) used a ρ_4 of 2430 kg/m^3 in the OOC model for the prediction of oil content in sediments. The organic fractions in *SS* (ϕ_5) and sediments (ϕ_4) determine the fugacity capacities (Z). Kranck et al. (1992 and 1996) have suggested that individual clay and silt particle (<100 μm) may flocculate in the marine system due to the biologically facilitated environment. The organic fraction in *SS* is reported in the range of 0.12 to 0.32. The organic fraction in sediments (ϕ_4) is reported in the range of 0.035 to 0.045 (Mackay and co-workers).

Physical processes including sediment burial and resuspension and *SS* deposition rates establish the pollutant concentration in water and sediments. The advection/burial rate (u_B) for sediments is reported in the range of 0.19 to 4.36 gm/m^2/day (Diamond et al., 1994; Diamond, 1999; and Ling et al., 1993). For the density of dry sediment of 2500 kg/m^3, the burial rates are estimated to be in the range of 0.003 to 0.064 cm/yr. Mackay et al. (1992) have also reported burial rates as high as 1.75 cm/yr in a lake system.

The resuspension rate (U_{10}) reported in the lake system varies from 0.5 to 13.5 gm/m^2/day. The U_{10} becomes equal to 0.007 to 0.2 cm/yr for a sediment density of 2500 kg/m^3 (Table 3.2). Sleath (1984) has summarised more than 25 different relationships for initial movement of sediment bedloads. Huang (1992) has also performed laboratory experiments for resuspension of drilling waste and developed an equation for mass flux as a function of advection velocity (u), and densities of water (ρ_2) and sediment (ρ_4). For ρ_2 = 1000 kg/m^3, ρ_4 = 2500 kg/m^3, resuspension coefficient (ξ) = 0.002 to 0.005 and current velocity (u) = 1.8 cm/sec, the resuspension rate (U_{10}) may vary from 0.0085 to 0.021 cm/yr The details of these models are given in Table 3.2.

Table 3.2. Physical properties of primary compartments (media) and their components

Primary Medium	Components	Volume fraction (v)	Density (kg/m^3) (ρ)	Organic fraction (ϕ)	Advection rate/Burial rate (u)	Depth (m)	Resuspension (U_{10})	Deposition (U_9)
Water Column (2)	*SS* (5)	$^{a}5 \times 10^{5}$ $^{b}5 \times 10^{6}$ $^{f}0.5\text{-}2 \times 10^{5}$ $^{g}2.08 \times 10^{7}$ $^{h}4.63 \times 10^{7}$ $^{i}>10 \times 10^{6}$	$^{a}1500$ $^{c}1800$ $^{g,h}2400$ $^{h}2000$ $^{k}1850$	$^{a,g}0.2$ $^{c}0.24\text{-}0.32$ $^{h}0.12$	$^{d,i}u = 1.8$ cm/s	95m ^{i}Grand Banks	$^{d}2.0 \times 10^{7}$ m/hr (0.18 cm/yr) ^{c}1-13.5 (g/m^2/day) ^{f}0.5 (g/m^2/day) ^{h}1.63 (g/m^2/day) For ρ_4 = 2500 kg/m^3, the resuspension rate varies from 0.007 to 0.2 cm/yr	$^{d}5.0 \times 10^{7}$ m/hr (0.44 cm/yr) ^{c}5-15 (g/m^2/day) ^{f}1.5 (g/m^2/day) ^{h}6.0 (g/m^2/day) For ρ_2 = 1800 kg/m^3, the deposition layer thickness formation rate varies from 0.03 to 0.31 cm/yr
	Water (2)		1003					
	Fish (6)	$^{a}1 \times 10^{6}$	$^{a}1000$	Lipid content			^{j}Huang (1992) has proposed ε (mg/cm^2/hr) = 2.64(τ-τc)$^{1.19}$ Assuming $\tau c = 0$ $\tau = \rho_2 \times \xi \times u^2$ $\rho_2 = 1.003$ g/cm^3 $\xi = 0.002 - 0.005$ $u = 1.8$ cm/sec ε/ρ_4 (cm/hr) = U_{10} $\rho_4 = 2.5$ g/cm^3 $U_{10} = 0.0085$ to 0.021 cm/yr	^{j}Huang (1992) has proposed $^{j}\omega_s$ (μm/sec) = $0.145 \times \delta^{1.58}$ where, $\delta = 10 - 100\ \mu m$ Seaconsult (2000) has recommended for $\delta > 100\ \mu m$ ω_s (m/sec) = $4.2(\delta)^{0.5}$, (δ) is in m for $\delta < 100\ \mu m$; ω_s (m/sec) = 0.0012 ω_s = U_9 (m/hr) ^{l}Sleath (1984) has recommended for $\delta > 100\ \mu m$ ω_s (m/sec) = $A \times (\delta)^{0.5}$, (δ) is in m $A = 2.8$ to 6.5 for $\delta < 100\ \mu m$ ω_s (m/sec) = $(92 \times 10^4) \times (\delta)^2$, ($\delta$) is in m
Sediment (4)	Pore water (2)	$^{a}0.7$ $^{g}0.85$ $^{h}0.915$ $^{k}0.4$ $^{l}0.35\text{-}0.5$	1003		^{e}0.19-0.7 (g/m^2/day) ^{f}0.3 (g/m^2/day) ^{h}4.36 (g/m^2/day)	$^{a}0.10$ $^{b}0.05$ $^{g}0.005$ $^{c}0.04 - 0.09$ $^{k}0.08$		
	Sediment solids (4)		$^{b,c}2000$ $^{g}2400$ $^{h}2640$ $^{k}2596$ $^{m}2430$	$^{a}0.04$ $^{g}0.0359$ $^{h}0.0447$	Assuming ρ_4 = 2500 kg/m^3, the burial rate (u_B) varies from 0.003 to 0.064 cm/yr ^{e}1.75 cm/yr			

a Mackay et al. (1992)
b U.S. EPA (1999b)
c Brandsma (1996)
d Sadiq et al. (2000)

e Diamond et al (1994)
f Diamond (1999)
g Mackay and Diamond (1989)
h Ling et al. (1993)

i Terra Nova (1996)
j Huang (1992)
k Seaconsult (2000)
l Sleath (1984)
m Brandsma (1996)

Mackay and co-workers have also reported the deposition rates in the range of 1.5 to 15 gm/m^2/day for a lake system. The estimated thickness of the material deposited may vary from 0.03 to 0.31 cm/yr for a *SS* density of 1800 kg/m^3 (Table 3.2). Mackay et al. (1992) have also reported a high deposition rate of 0.44 cm/yr. Seaconsult (2000) used a particle tracking technique to determine the fate of synthetic based fluids. They have recommended that particles of size (δ) smaller than 100 μm, will form flocs due to the presence of phytoplankton and other organic substances and will settle with a constant fall velocity of 100 m/day (or 0.00761 cm·s^{-1}). Huang (1992) has performed experiments to determine the fall velocity of suspended particles of diameter (δ) less than 100 μm. He recommended that the particles of size bigger than 100 μm will settle with a fall velocity of $4.2(\delta)^{0.5}$. Sleath (1984) has proposed the multiplication coefficient (A) in the range of 2.8 to 6.5 instead of 4.2 depending on the shape of a settling particle. The details of various deposition models are given in Table 3.2.

For determining the advection rate in the water column and the resuspension rate on the seabed, current velocity (u) is used. Brandsma (1996) used a constant value, which is the root mean square (RMS) of velocities over the cross-sectional area. He employed this assumption for the OOC model for predicting the fate of oil-based drill cuttings in the North Sea. The current speed is highly variable in intensity and direction. It is a site-specific characteristic and the focus of this research is the East Coast of Canada. Terra Nova (1996) has reported a mean current speed of 3.6 cm·s^{-1} at the surface and 1.8 cm·s^{-1} at mid depth on the East Coast of Canada (Newfoundland). Sadiq et al. (2001a-c) have also used a mean current speed (u) of 1.8 $cm \cdot s^{-1}$ for hypothetical case studies in the Newfoundland offshore.

3.2. MODEL CHARACTERISATION

After defining the pollutants and media characteristics, the water sediment interaction model formulation can be applied to determine the fate of pollutants in the water column and sediment pore water. To use a parametric approach in probabilistic analysis, the input variables are expressed in terms of statistical distributions. The statistical distributions are defined subjectively based on available data as discussed in the previous section. Monte Carlo (MC) simulation using Latin Hypercube Sampling (LHS) is proposed for performing uncertainty analysis. To perform the MC simulations in the fate modeling process some assumptions are made. A brief description of the selection of distributions and MC simulation methods is also presented in this section.

3.2.1 MODEL ASSUMPTIONS

A marine system is a complex environment in which various processes are occurring simultaneously. A water sediment interaction model considers some of the important physico-chemical processes to determine the fate of pollutants in the water column and sediments. Therefore, the following assumptions are made to simplify the complex processes occurring in the marine environment:

1. The water sediment interaction model is a steady state model and therefore continuous pollutant loading rates are assumed (Meinhold, 1998).

2. In the fate modeling, the impact area (A_W) is predefined to estimate the pollutant concentrations in the water column and pore water. The impact area (A_W) is defined by a radius (R), which is the radius of a circle whose area equals to the impact area Brandsma (1996).

3. The water column depth (d_W) is fixed to determine the mixing control volume for pollutants (Figure 3.3). In this case the value is taken at 95 m (Terra Nova, 1996).

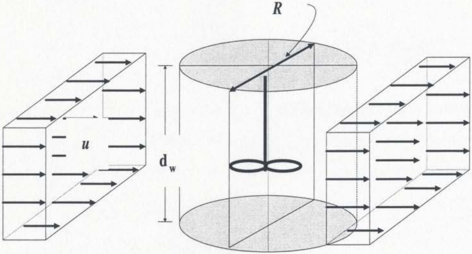


Figure 3.3. Control volume and uniform velocity profile (not to the scale)

4. Mid depth velocity (u) is assumed to be a representative velocity, which has a uniform profile over the cross section (boundary layer effects are not considered). The volume flow rate (G) can be determined by multiplying cross-sectional area with the advective velocity (u). The projected cross-sectional area of the control volume is the product of the depth of water column (d_W) and the diameter ($2R$) of the impacted area.

5. The pollutants entering the control volume are assumed to be completely mixed under steady state conditions and physico-chemical processes are taking place uniformly over the impact area (A_w).

6. Depending on the general characteristics of the drilling waste, part of the pollutant loads is assumed to go directly into the sediments (E_4) and the remainder disperses in the water column (E_2) and settles according to the particles' settling velocities.

7. Floc formation at the concentrations of fine cuttings is quick and assumed to be an instantaneous process with floc diameters of 100 μm or more while settling. The larger cuttings of ≈ 1 mm may take 8 to 18 minutes to settle for a depth of 95 m water column (Sleath, 1984). Therefore drill cuttings larger than 1 mm are assumed to settle immediately, which account for the pollutant loading going directly into the sediments (E_4). In this analysis a conservative approach is adopted: 20% of the load is assumed to be attached to bigger particles that go directly to sediments, while the remainder settles at their corresponding settling velocities.

The following section will discuss various types of uncertainties involved in fate modeling and MC simulation methods used in estimating uncertainties. A detailed description of the selection of statistical distributions used for input variables to the water sediment interaction model is also presented.

3.2.2. UNCERTAINTIES - ESTIMATION METHODS

Uncertainties are inherent in modeling processes, and include natural randomness, uncertainty associated with the model parameters, and the model's structure. Natural randomness/heterogeneity includes spatial and temporal fluctuations inherent in natural processes. The structure of mathematical models that are employed to represent scenarios and processes of interest is often a key source of uncertainty, due to the fact that models are only a simplified representation of a real-world system (Cullen and Frey, 1999). Model uncertainties are not significant in a well-tested physical model like fugacity and aquivalence based models (CCME, 1997).

Quantities that are inherently variable over time, space or some population of individuals are referred to as variability or Type A uncertainty. This variability cannot be reduced, as it is the inherent quality of the system. Another type of uncertainty is called lack of knowledge uncertainty, subjective or Type B uncertainty. The variability is the property of the system being studied and uncertainty is the property of the analyst or instrument (Cullen and Frey, 1999).

To estimate the uncertainty in the model's parameters and structure, various simulation techniques are used (Ang and Tang, 1984). The methods for simulating the propagation of probability distribution through inputs in a model are based upon random sampling. The most well known method is MC simulations using Latin Hypercube Sampling (LHS). Some transformation techniques, which are not based on MC simulations, are also used in propagating distribution. The taxonomy of commonly used methods for propagating moments and distributions through models are summarized in Table 3.3.

Table 3.3. Common probabilistic methods for propagating moments and distributions (Cullen and Frey, 1999)

Group	Methods
Analytical Solutions for Moments	• Central limit theorems • Properties of mean and variance
Analytical Solutions of Distributions	• Transformation of variables
Approximation Methods for Moments	• First-order methods • Taylor series expansions
Numerical Methods	• Simple MC simulation • *Latin Hypercube sampling* • Importance sampling • Fourier amplitude sensitivity test • Others

Monte Carlo refers to the traditional method of sampling random variables in simulation modeling. Samples are chosen completely randomly across the range of the distribution, thus necessitating large numbers of samples for convergence for highly skewed or long tailed distributions (Palisade, 1997). Figure 3.4 describes the general procedure of MC simulation technique in which samples from two independent input variable distributions x_1 and x_2 are selected randomly. The output distribution z is calculated using a relationship of input variables e.g., in Figure 3.4 output (z) is a product of variables x_1 and x_2.

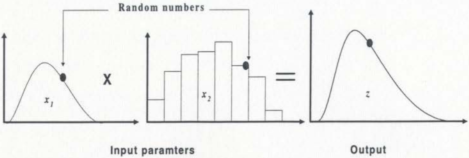


Figure 3.4. A random sampling process of simple or ordinary MC simulations

Many variations of the MC simulation technique are aimed at reducing the computational effort and improving statistical techniques. A review of the literature on the use of MC simulation in environmental engineering shows that the LHS method is the only variance reduction technique that is widely used (Cullen and Frey, 1999). The use of MC methods in the uncertainty analysis especially in the area of risk assessment and fate modeling has received growing attention in recent times. The MC simulation method has been proposed as the method of choice due to the robustness of the method and its ability to handle non-linearity of the problem (U.S. EPA, 1996a). As a result, MC simulation is the most widely used methodology to account for uncertainties in contaminant fate modeling.

The input parameters are not necessarily independent of each other. The correlation coefficients can also be defined in MC simulations to account for the inter dependence of input parameters. The estimation of correlation coefficients is data intensive but subjective judgments may also be used. This is one of the major drawbacks of using MC simulations. In the absence of enough evidence, independent input parameters are assumed. Trial and error methods are also used in which different values of correlation coefficients are assumed to perform MC simulations (Hammonds et al., 1994).

The U.S. EPA (1996a) has recommended LHS over simple random sampling for complex models due to better performance. The LHS is a relatively new sampling technique used in simulation modeling (Palisade, 1997). It is designed to accurately recreate the input distribution through sampling in fewer iterations when compared with the simple MC simulations. The key to LHS is stratification of the input probability distributions. Stratification divides the cumulative curve into equal intervals on the cumulative probability scale (0 to 1). A sample is then randomly taken from each interval or stratum of the input distribution. Sampling is then forced to take values from each interval to recreate the input probability distribution. It offers great benefits in terms of increased sampling efficiency and faster run times (Morgan and Henrion, 1990).

3.2.3 SELECTION OF STATISTICAL DISTRIBUTION

The distributions may result directly from data obtained from proper experimental design, but in the absence of data usually subjective judgement must be used to show the degree of belief that the unknown value of a parameter lies within a specified range (Hammonds et al., 1994). When data are limited but uncertainty is relatively low (less than a factor of 10), a range may be used to specify a uniform distribution. If there is knowledge about the most likely value (MLV) or mode, in addition to range, a triangular distribution may be assigned. When the uncertainty range exceeds a factor of 10, it is often prudent to assume a probability distribution of the logarithms of parameter values; therefore, when the range of uncertainty is very large, a log-uniform, log-triangular distribution may be more appropriate than the uniform or triangular distribution (Hammonds et al., 1994). The other important commonly used distributions are normal, lognormal, exponential and/or empirical distributions. These are usually dependent on the availability of relevant data. The most commonly used probability density functions (PDF) of some statistical distributions are shown in Figure 3.5.

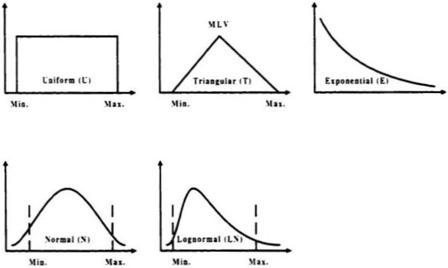


Figure 3.5. PDFs of some commonly used statistical distributions

The statistical distributions like uniform (U), triangular (T), exponential (E), normal (N), and lognormal (LN) distributions are defined for various input variables in this research. The truncated forms of normal and lognormal distributions are also defined where minimum and maximum bounds are known. Table 3.4 provides a summary of proposed statistical distributions for physical properties of media and their characteristic parameters.

Table 3.4. Proposed statistical distribution for multimedia properties

Inputs	Statistical distribution	Min.	μ or MLV	σ	Max.	Comments
Δ *or* d, (m) sediment depth	Triangular	0.04	0.08		0.09	Sleath (1984); Seaconsult (2000)
v_d pore water fraction	Triangular	0.35	0.4		0.5	
[*]v_s (ppmv) *SS* volume fraction	Triangular	0.2	20		50	Various sources (see in the text)
ϕ_d Sediments organic fraction	Uniform	0.035			0.045	Timothy and David (2000)
ϕ_s *SS* organic fraction	Uniform	0.12			0.32	Various sources (see in the text)
ρ_d (kg/m^3) density of sediments	Triangular	2000	2500		2640	
ρ_s (kg/m^3) density of *SS*	Triangular	1500	1800		2400	
u (cm/sec) advective velocity	Exponential		1.8			Sadiq et al. (2000a-d)
u_B (g/m^2/day) burial rate	Uniform	0.19			0.70	Diamond (1999)
ξ coefficient of resuspension	Uniform	0.002			0.005	Huang (1992)
δ (μm) *SS* diameter	Truncated Lognormal	100	200	150	1000	Sleath (1984); Seaconsult (2000)
A coefficient for deposition	Triangular	2.8	4.2		6.5	

[*] ppmv: parts per million by volume

Statistical Distributions for Media Properties

Brandsma (1996) has suggested that the mixing depth of sediment (Δ) on the seabed may vary from 4 to 9 cm. but Seaconsult (2000) has recommended a depth of 8 cm for determining the base oil concentration. A triangular distribution (T) is assumed with a minimum value of 4. most likely value (MLV) of 8 and maximum value of 9 cm. It can be designated by T (4.0. 8.0. 9.0).

The volume fraction of *SS* (v_5) is mostly reported in the range of 0.2 to 50 ppmv (Mackay and co-workers) although a value as high as 2770 ppmv is also reported (Terra Nova. 1996). This high value is neglected due to lack of evidence. A triangular distribution is assumed for v_5. which has a minimum value of 0.2. mode (MLV) of 20 and a maximum value of 50 ppmv. The pore volume fraction (v_4). or porosity ranges from 0.35 to 0.5 in seabed sediments (Sleath. 1984). Seaconsult (2000) assumed a constant value of 0.4. A triangular distribution is assumed with minimum and maximum values of 0.35 to 0.5. respectively. An MLV (or mode) of 0.4 is recommended. The proposed triangular distribution can be designated by T (0.35. 0.4. 0.50).

The organic fractions in *SS* (ϕ_5) and sediments (ϕ_4) are assumed to be uniformly distributed (U) using minimum and maximum values available in the literature. Timothy and David (2000) have recommended a uniform distribution for defining the organic fraction in the food web modeling. The ϕ_5 is defined by U (0.12. 0.32). where 0.12 and 0.32 are minimum and maximum values. respectively. Similarly. the organic fraction in sediments (ϕ_4) is defined by U (0.035. 0.045).

The densities of *SS* (ρ_S) and sediments (ρ_d) are assumed to be triangularly distributed. The ρ_S is defined by T (1500, 1800, 2400). The density of sediment (ρ_d) is defined by T (2000, 2500, 2640). The minimum and maximum values are defined based on recommendations by Seaconsult (2000) and U.S. EPA (1999b). The most likely value (MLV) is calculated by taking the average of two intermediate values (Table 3.2).

The advective velocity (u) is defined by exponential distribution (E) with a mean current speed of 1.8 cm/sec (Sadiq et al., 2001a-d). The burial rate (u_B) of sediment varies from 0.003 cm/yr (0.19 g/m^2/day) to 0.064 cm/yr (4.36 g/m^2/day). A value as high as 1.75 cm/yr is also reported in the literature, but ignored due to lack of evidence. A uniform distribution with a range of 0.19 to 0.7 g/m^2/day is used (Diamond, 1999) for a conservative assessment of pollutant concentration in sediments (Table 3.4).

To estimate the resuspension rate (U_{10}), the resuspension coefficient (ξ) is defined by uniform distribution U (0.002, 0.005), as proposed by Huang (1992). To determine the deposition rates of drill cuttings with *SS* flocs, a methodology proposed by Seaconsult (2000) is adopted, which states that the fine particles make flocs of 100 μm or more before settling. The multiplication coefficient (A) of the settling equation (Table 3.2) is also defined by a triangular distribution, T (2.8, 4.2, 6.5) (Sleath, 1984).

The particle size distribution of drill cuttings shows that approximately 45% are fines (< 250 μm), 5% medium sand (250 - 500 μm), 20% coarse sand (500 μm - 1 mm) and 30% are of bigger size pebbles (Seaconsult, 2000; Sleath, 1984). Particle size (δ) is generally defined by lognormal distribution in the soil and fluid mechanics literature. A lognormal distribution (LN) is assumed with a mean and standard deviation of 200 μm and 150 μm, respectively. The lognormal distribution is truncated at the upper and lower bounds of 1000 μm and 100 μm, respectively. The cuttings of larger than 1 mm are assumed to settle immediately, which accounts for an assumed 20% of total pollutant loadings going directly into the sediments (E_4) (Sadiq et al., 2001d).

Statistical Distributions for Physico-chemical Characteristics of Pollutants

The statistical distributions for physico-chemical characteristics of pollutants are summarized in Table 3.5. In the case of organic pollutants, statistical distributions of Henry's coefficient (H) and half-lives in water ($H_{1/2}$) and sediments ($H_{1/2\sigma}$) are defined. The half-lives are derived based on anaerobic biodegradation rates in water and sediments. Henry's coefficient (H) for ester is calculated based on QSAR (Lyman et al., 1990). A uniform distribution is assumed, which is designated by U (0.1, 0.15). Henry's coefficient (H) for naphthalene ranges from 42 to 56 and a uniform distribution is assumed. The K_{OC} for naphthalene is assumed to be uniformly distributed and designated by U (400, 1000). The half-lives of both organic pollutants are assumed to be normally distributed with lower and upper bounds truncated at reported minimum and maximum values, respectively. Ester mass transfer (U_s) through diffusion is calculated by QSAR (Lyman et al., 1990). The diffusion coefficient (D_{sw}) is divided by path length or mixing depth (Δ) to calculate U_s. For all other pollutants under consideration, U_s is assumed to be triangularly distributed and designated by T (1, 2, 4) × 10^{-4}.

Table 3.5. Proposed statistical distribution for physico-chemical properties of selected pollutants

Organic pollutants	H (m^3·pa/ mol)	K_{ow} or K_{oc}	$MT\ (U_s)$ (m/hr)	$H_{1/2}$ (days)	$H_{1/2\sigma}$ (days)
Esters	U (0.1, 0.15)	$K_{ow} = 49$ point estimate	D_{gw}/Δ	[2]TN (50, 20, 12, 130)	TN (20, 2, 16, 22)
Naph.	U (42, 56)	For K_{oc} U (400, 600)	T[3] (1, 2, 4) × 10^{-4}	TN (10, 5, 0.5, 20)	TN (150, 50, 25, 258)
Heavy Metals	[1]$LogK_\sigma$ (L/kg)	[1]$LogK_\pi$ (L/kg)		$H_{1/2}$ (days)	$H_{1/2\sigma}$ (days)
Pb	TN (4.6, 1.9, 2.0, 7.0)	TN (5.7, 0.4, 3.4, 6.5)			
Hg	TN (4.9, 0.6, 3.8, 6.0)	TN (5.3, 0.4, 4.2, 6.9)		T (25, 1000, 2000)	64 years point estimate
As	TN (2.4, 0.7, 1.6, 4.3)	TN (3.9, 0.5, 2.0, 6.0)			
Cu	TN (3.5, 1.7, 0.7, 6.2)	TN (4.7, 0.4, 3.1, 6.1)			
Zn	TN (4.1, 1.6, 1.5, 6.2)	TN (5.0, 0.5, 3.5, 6.9)			
Cr	TN (4.9, 1.5, 1.9, 5.9)	TN (5.1, 0.4, 3.9, 6.0)			
Cd	TN (3.3, 1.8, 0.5, 7.3)	TN (4.9, 0.6, 2.8, 6.3)			
Ni	TN (3.9, 1.8, 0.3, 4.0)	TN (4.4, 0.4, 3.5, 5.7)			

[1] U.S. EPA (1999c) has defined the distribution and parameters

[2] TN (mean, stdev., min., max.)

[3] T (min., MLV, max.)

For heavy metals half-lives are not important except for Hg, which exists in various forms. The half-life of Hg in water is designated by a triangular distribution T (25,1000,2000). In aquivalence based models, the most important parameters are K_π and K_σ, which define the metals partitioning with *SS* and sediments, respectively. The U.S. EPA (1999c) collected information from more than 250 sources to define the ranges and statistical distributions of heavy metal partitioning coefficients. The $LogK_\pi$ and $LogK_\sigma$ are normally distributed and are truncated at minimum and maximum bounds. The details of the statistical distributions and their characteristic parameters are given in Table 3.5.

3.3 PROBABILISTIC ANALYSIS

After defining the statistical distributions for model inputs the immediate objective of this research was to perform MC simulations to determine the model outputs. The outputs of the model were pollutant concentrations in the water column (C_w) and sediment pore water (C_{PW}). The uncertainty/variability in the model inputs contributed to the uncertainty in model outputs.

The uncertainty in the model structure due to simplification of the processes was not addressed in this research (CCME, 1997). The fugacity/aquivalence model structure developed in Table 2.10 (Chapter 2) was converted into the spreadsheet format as shown in Figure 3.6. The @Risk (Palisade, 1997) software was used for MC simulations. The software is an add-on to Microsoft Excel. The input parameters were defined by probability density functions (PDF).

The MC simulations were performed for different predefined impact area (A_w) and operational pollutant loading rate (E_i) conditions. The concentrations of each pollutant in the water column and pore water were determined under a given discharge condition. The simulations were then repeated for another set of conditions defined by a different impact area and/or pollutant loading rate. The model outputs - water column (C_w) and sediment pore water (C_{PW}) concentrations - were obtained in the form of an empirical distribution function (EDF). The EDFs of model outputs were fitted to various candidate distributions. The parameters of the best-fitted distribution were determined for each discharge condition. The predicted environmental concentration (*PEC*) was determined by defining a higher percentile level of a concentration which is generally 90th or 95th percentile value on fitted distributions (Lenwood et al., 1998). Further, multiple linear regression analysis was performed to develop empirical regression models for parameters of the fitted distribution (e.g., mean and standard deviation) for each pollutant separately as function of their pollutant loading rates (E_i) and radius of impacted area (R).

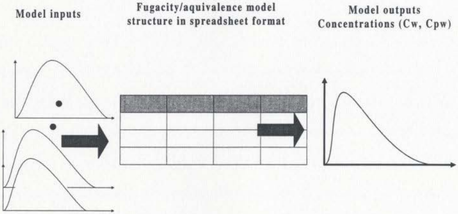


Figure 3.6. The MC simulations for fate modeling in the spreadsheet format

3.3.1. OPERATIONAL DISCHARGE CONDITIONS

The range of pollutant loading rates can be defined based on their emissions in various jurisdictions, which include the Gulf of Mexico (GOM), California, Alaska and the East Coast of Canada. The base fluid (ester) constitutes approximately 47% of the SBF's weight. The average weight of cuttings produced from a model deep development well is approximately 350 metric tones (MT). For the case of 10% attached fluids, 45 MT (57 m^3) of ester as a base fluid goes into the ocean system from a single well. The ester quantity is reduced to 16 MT for 4% attached base fluid (U.S. EPA, 1999b).

The loading rates were selected such that all practical discharge conditions would be covered, e.g., for 15% attached base fluid, the discharge rate of ester will be 108 kg/hr (in the case of a one month drilling time). The discharge rate decreases to 26.4 kg/hr for the 5% attached base fluid case (Sadiq et al., 2001b). The discharge rates of ester in the ocean environment were selected in the range of 5 to 150 kg/hr.

Similarly, heavy metals and naphthalene loads can be calculated based on the composition of stock barite used in the SBFs and formation oil contamination, respectively. The heavy metals As, Cd, Cu, Hg, Ni and Pb are found in low concentration in barite (< 35 mg/kg of barite). Sadiq et al. (2001c) calculated As and Cu pollutant loadings rates which were below 1.2 g/hr for 15% attached base fluid. The naphthalene is an indicator for the formation oil contamination and only traces are expected in synthetic base drilling waste. The loading rates for these pollutants were selected within the range of 0.025 to 3 g/hr to cover all practical ranges. The Cr and Zn are generally found in higher concentration in stock barite (> 200 mg/kg of barite). The loading rates for these pollutants were selected within the range of 0.10 to 30 g/hr. The mass balance analysis for calculating the specific pollutant loading rates for our discharge scenarios is provided in Chapter 7 of this thesis.

The concentrations in the water column and pore water also depend upon the total impact area (A_w) which is defined by an equivalent circular area of radius R. Information about impacts of SBFs from field investigations is limited in comparison to WBFs. The U.S. EPA (1999b) has summarized a few field studies of SBFs' impact. The studies related to SBFs in which ester was used as a base fluid. They are summarized in Table 3.6. For various locations in the North Sea the SBFs were detected only in the upper 10 cm of sediment to a distance of 200 m from the point of discharge.

Daan et al. (1996) have reported an increase in ester concentration with increase in distance. The measured concentration increased from 393 to 834 mg/kg at distances of 75 m to 125 m from the point of discharge. The authors have surmised that this happened due to resuspension, and contaminated heterogeneous sediment near the outlet was spread out and well mixed over a larger area. This study also noted that the effects at 500 m and 3000 m were recovered after 11 months. In another study by Schaanning (1995), the sediment ester concentration decreased logarithmically with distance from discharge point. Benthic organisms were severely affected within a 100 m radius.

The U. S. EPA (1999b) has concluded that there is a little evidence of biological impacts at over 500 m from the point of discharge. The impact on sediment is expected to be within 100 m to 200 m from the point of discharge. The ester based SBFs are readily biodegradable in comparison to other fluids. The U.S. EPA (1999b) also concluded that the recovery of impacted benthic life starts within a one-year time.

Table 3.6. Seabed filed studies for Ester based drilling fluids

Study source and location	*dw* (m)	Cuttings/ SBFs discharged	[a]*R* (m)	[b]*C* (mg/kg)	[c]Time (months)
Daan et. al (1996) North Sea/ Dutch continental shelf	30	361 m^3 SBFs; 180 Metric tones (MT) ester	75	706	1
			75	393	4
			75	84	11
			125	300	1
			125	834	4
			125	10	11
			200	54	1
			200	161	4
			200	55	11
Smith and May (1991); Schaanning (1995) North Sea/ Norwegian continental shelf	67	749 MT cutting; 96.5 MT ester	50	85.300	1
			100	46.400	1
			200	208	1
			50	0.21	
			100	0.22	
			200	1.34	
Vik et al. (1996) Loke	76-81	180 MT SBFs	250	93	1
			500	5	1
			250	10	12
			500	5	12
Vik et al. (1996) Sleipner A	76-81	399 MT SBFs	250	50	1
			500	20	1
			250	25	12
			500	<5	12
Vik et al. (1996) Sleipner Ø		380 MT SBFs	250	400	
			500	30	
U.S. EPA (1999b) GOM continental slope	565	6263 bbl (ester + LAO)	75	165.051	(prior to 1997)
		1486 bbl additional fluid	75	198.320	(prior to 1998)

[a]distance from point of discharge; [b]concentration of base fluid in dry sediments ; [c]time of sampling after discharge

Based on the available information for each pollutant, the loading rates were defined at three levels corresponding to five different levels of impact radius (*R*). Therefore MC simulations were performed for 15 different discharge scenarios for each pollutant. For example for ester, the first simulation trial was performed at a loading rate of 150 kg/hr assuming that the area impacted was within a radius of 50 m. In the second trial, an impact radius of 100 m was defined. The impact radius is increased in steps to 5 km for the 5th trial at the same loading rate. Then the loading rate was changed from 150 to 75 kg/hr for the 6th trial. For this loading rate the same procedure was repeated. Similarly for other pollutants, three pollutant loading rates were defined for five impact radii values. Table 3.7 summarizes the loading rates of different pollutants (E_i) and impact radius (R) for performing MC simulations on the fugacity/aquivalence based water sediment interaction model.

Table 3.7. Various discharge scenarios and trials for MC simulations

Simulation Trials	R (km)	Ester	As, Cd, Cu, Ni, Hg, Pb and naphthalene	Cr and Zn
		E_i (kg/hr)	E_i (mg/hr)	
1	0.05	150	3000	30000
2	0.10	150	3000	30000
3	0.50	150	3000	30000
4	1.00	150	3000	30000
5	5.00	150	3000	30000
6	0.05	75	1000	10000
7	0.10	75	1000	10000
8	0.50	75	1000	10000
9	1.00	75	1000	10000
10	5.00	75	1000	10000
11	0.05	5	25	100
12	0.10	5	25	100
13	0.50	5	25	100
14	1.00	5	25	100
15	5.00	5	25	100

3.3.2. MC SIMULATIONS

The MC simulations using the LHS method were performed for the fugacity/aquivalence models. For each simulation, 10,000 iterations were performed to estimate concentrations in multimedia environment. The inputs of the models were defined by the statistical distributions as described in section 3.2.3. The results of MC simulations for fugacity and aquivalence models are discussed separately in this section.

Fugacity Models

The MC simulations for ester and naphthalene were performed using a fugacity model. Simulation results for ester are discussed in detail here. In the first trial for ester, the loading rate and impact radius were 150 kg/hr and 50 m, respectively. The outputs of interest in the model simulations were concentrations in multimedia. The model outputs - water column concentration (C_w) and pore water concentrations (C_{PW}) - were obtained in the form of an empirical distribution function (EDF). For first trial, the distribution of C_w is shown in Figure 3.7. The ester water column concentration is provided in the form of a histogram. The 95th percentile of concentration is also shown with the help of a solid line. The ester water column concentration may vary from 0.2 to 4 μg/L for the first trial. The mean and median values of C_w are 0.94 and 0.84 μg/L, respectively. This shows a slight positive skew in the distribution. The standard deviation of water column concentration is 0.41 μg/L. The maximum value of water column concentration is approximately 20 times more than the minimum value. The 95th percentile of the C_w is 1.78 μg/L, which is less than half of the maximum value (4 μg/L). It implies that only 5% of the values lie within the range of 1.78 to 4 μg/L.

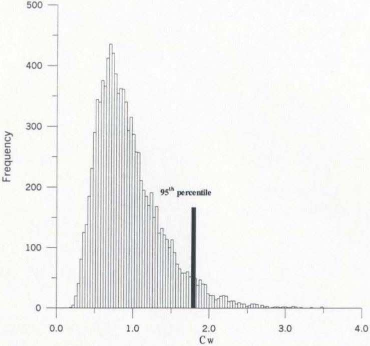


Figure 3.7. Histogram of water column ester concentration (μg/L) for Trial 1

The second output of the simulations was the pore water concentration (C_{PW}). The histogram of pore water concentration is shown in Figure 3.8. The C_{PW} varies from 6.62 to 23.9 g/L. The mean and median values are 11.8 and 11.3 g/L, respectively. The standard deviation of water column concentration is 2.52 g/L. The minimum value of pore water concentration is approximately 4 times less than its corresponding maximum value. The C_{PW} distribution is also positively skewed. The 95th of pore water concentration is 16.8 g/L.

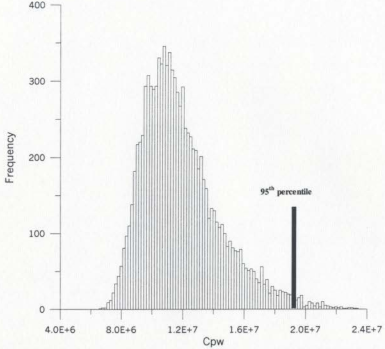
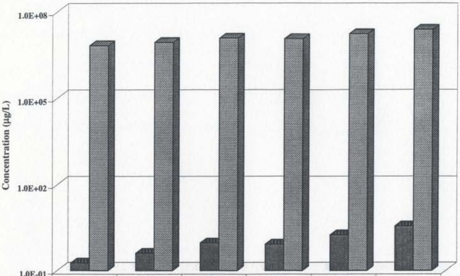


Figure 3.8. Histogram of pore water ester concentration (μg/L) for Trial 1

Figure 3.9 is a plot showing a comparison of water column and pore water concentration at various percentiles. The concentrations are compared at 5th, mean, 50th (median), 95th and their maximum values. The pore water concentration is higher than the water column concentration by various order of magnitudes. The 95th percentile of C_{PW} is more than C_W by approximately 7 orders of magnitude. Higher uncertainty is observed in the C_W values, which may be due to the higher settling rate of drill cuttings and higher uncertainty in half-life of ester in water (12 to 130 days).



	Min.	5%	Mean	50%	95%	Max.
■ Cw	1.87E-01	4.07E-01	9.32E-01	8.40E-01	1.78E+00	3.58E+00
▨ Cpw	6.62E+06	8.55E+06	1.18E+07	1.13E+07	1.68E+07	2.39E+07

Figure 3.9. Comparison of water column and pore water ester concentrations in (Trial 1)

The higher pore water concentration implies higher fugacity (f_4) in comparison to water column fugacity (f_2). Base fluids are hydrophobic in nature and may try to attach themselves with sediments. Due to the density and particle sizes of drill cuttings, a major portion of the drilling waste settles to the seabed sediments. Under steady state conditions the contaminants start leaching into the pore water and maintain higher levels of concentration in comparison to water column concentration. The MC simulations are also performed for naphthalene in the fugacity model. The MC simulation results for all trials are summarized in section 3.4.2.

Aquivalence Models

The aquivalence based model is used for predicting heavy metals (As, Cd, Cu, Cr, Pb, Hg, Ni, and Zn) concentration. The MC simulations were performed for each metal separately. The MC simulation results from the first trial for Cd are presented and discussed in detail. The summary of simulations is given for each pollutant in the section 3.4.2.

The first MC simulation trial for Cd was performed at a loading rate of 3g/hr and an impact radius of 50 m. The water column concentration of Cd varies from 4.45×10^{-8} to 7.61×10^{-3} μg/L. The mean and median (50th percentile) C_w are 6.77×10^{-5} and 1.16×10^{-5} μg/L, respectively. This shows a highly positive skew in the distribution. The standard deviation of the water column concentration is 5.01×10^{-5} μg/L. The 95th percentile of the C_w is 3.32×10^{-4} μg/L, which is approximately 20 times less than the maximum value. The minimum value of the water column concentration is approximately 5 orders of magnitude less than the maximum value. The histogram of C_W is shown in Figure 3.10.

The results for the pore water concentration (C_{PW}) are shown in Figure 3.11. The C_{PW} may vary from 1.77×10^3 to 3.82×10^7 μg/L. The mean and median values of C_{PW} are 96.3×10^4 and 7.62×10^4 μg/L, respectively. The C_{PW} is also a highly positive skewed distribution. The standard deviation of the water column concentration is 2.64×10^6 μg/L. The 95th percentile value of C_{PW} distribution is 5.51×10^6 μg/L. The minimum value of pore water concentration is approximately 4 orders of magnitude less than its maximum value.

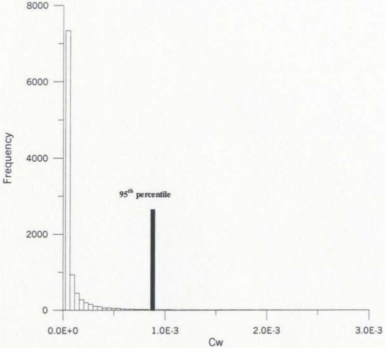


Figure 3.10. Histogram of Cd water column concentration (μg/L) for Trial 1

Figure 3.12 is plotted to compare water column and pore water concentrations at various percentiles. The concentrations are compared at 5th, mean, 50th (median), 95th and maximum values. The pore water concentration is more than the water column concentration by orders of magnitude. The pore water concentration is more than the water column concentration by approximately 10 orders of magnitude at their 95th percentiles. The uncertainty in the concentration outputs can be estimated by comparing their minimum and maximum values, which differ by 4 to 5 orders of magnitude.

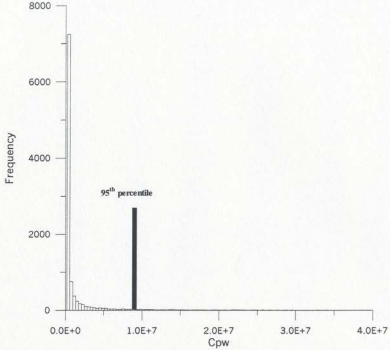
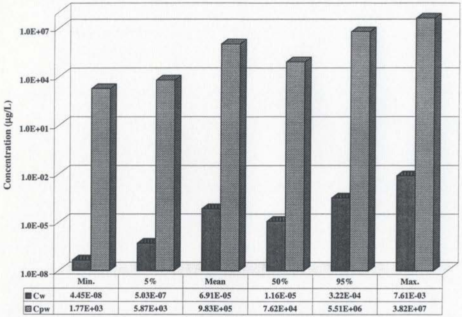


Figure 3.11. Histogram of Cd pore water concentration (μg/L) for Trial 1

The heavy metals maintain higher aquivalence (*A*) in sediments in comparison to the water column. Heavy metals are very persistent in nature and have practically infinite half-lives. Metal distribution in multimedia is a function of their partitioning abilities with sediments (K_σ) and particulates (K_π). The aquivalence based steady state model determines long-term leaching of metals into pore water. The biodegradation and decay of heavy metals is not expected, although oxidation reaction, speciation and other chemical reactions may be possible.



	Min.	5%	Mean	50%	95%	Max.
■ Cw	4.45E-08	5.03E-07	6.91E-05	1.16E-05	3.22E-04	7.61E-03
▨ Cpw	1.77E+03	5.87E+03	9.83E+05	7.62E+04	5.51E+06	3.82E+07

Figure 3.12. Comparison of Cd concentrations in water column and pore water (Trial 1)

3.3.3. SENSITIVITY ANALYSIS (SA)

Sensitivity analysis (SA) is the process of estimating the degree to which output of a fate model changes as values of input parameters are changed. The American Standard for Testing and Materials (ASTM, 1998) has recognized the role of SA in the fate modeling as follows:

1. SA can identify the input parameters that have the most influence on model output;

2. SA can identify the processes which have greatest influence on model output; and

3. SA can quantify the change in output caused by uncertainty and variability in the values of input parameters.

Sensitivity of the fate model is linked to input parameters through governing equations. The input parameters in probabilistic fate modeling may be represented by given ranges and/or distributions. Field investigations and monitoring can only provide the best site-specific estimate. There are several reasons for identifying key model inputs. which contribute to uncertainty in model outputs. An identification of significant contributors to output variance gives the analyst an awareness of which input variable is controlling the output results. The basic exploration of the models. inputs and results. promotes improved understanding and interpretation of the analysis (Culen and Frey. 1999).

In a probabilistic analysis. the majority of the variance in the output is attributable to variability and or uncertainty in a small subset of the inputs. There are varieties of methods of identifying key input variables from model outputs. These methods include the scatter plot. partial and rank correlation coefficients. multivariate regression. contribution to variance and probabilistic sensitivity analysis. These methods are discussed in detail in the literature. e.g. Iman and Helton (1988). and Culen and Frey (1999) and they are briefly discussed below.

A correlation coefficient is a measure of the degree of association or covariance between two random variables. Correlation coefficients provide an estimate of the linear dependence of a model output on a particular model input. Correlation coefficients are sensitive to the strength of the linear relationship between model inputs and output and the range of variation of input. Correlation coefficients are estimated based on sample values of both the inputs and output and their relative means.

$$\rho_c = \frac{\sum_{k=1}^{m}(x_k - \bar{x})(z_k - \bar{z})}{\left(\sum_{k=1}^{m}(x_k - \bar{x})^2 \sum_{k=1}^{m}(z_k - \bar{z})^2\right)^{1/2}} \tag{3.1}$$

where m is the sample size or number of iterations in the simulations. x is an input and z is an output. x_k and z_k are sample values of x and z. The value of correlation coefficient ρ_c may vary from -1 to +1 where:

$\rho_c = +1$, implies linear dependence, a positive slope (z increases as x increases)

$\rho_c = 0$, implies no linear dependence, a value of x provides no useful information about value of z, and

$\rho_c = -1$, implies linear dependence, a negative slope (z increases as x decreases)

For typical probabilistic simulations, correlation between an input and an output greater than |0.5| indicates substantial dependence of the variation in the output on variation of the input. Values as low as |0.2| also may be of interest, depending on the sample size. Larger correlation coefficients indicate less dispersion of sample values from an idealized linear relationship between input and output. Generally correlation coefficients are sensitive to both the strength of linear relationship between an input and output, and to the range of variation of the input (Culen and Frey, 1999).

If several values of the input or output are clustered together in a random pattern, and one point is located away from the cluster, an artificially high estimate of the correlation coefficient may result. Alternatively, in cases where underlying dependence is nonlinear (but monotonic), the sample correlation coefficient will underestimate the dependence. A way to avoid these problems is to calculate the correlation coefficient using the rank of both x and y. Each sample of a random variable has a rank. The rank is determined by ordering the sample values in ascending order. The lowest value has a rank one, the next lowest has a rank two and so on. The largest sample value has rank equal to the number of samples. The rank correlation coefficient is robust to different monotonic dependencies between input and output. A rank correlation coefficient correctly characterizes the strong nonlinear dependence by being equal to or almost equal to positive unity.

Another common method used for SA is to estimate the relative approximate contributions of each parameter to the variance of final outputs by squaring the rank correlation coefficients and normalizing them to 100% (Maxwell and Kastenberg, 1999). The parameters having the greatest effect are considered to be those for which additional data should reduce the amount of overall uncertainty in the results. Hammonds et al. (1994) and Maxwell and Kastenberg (1999) used this technique in human health risk assessment for identifying the key input variables. In the following section, SA using rank correlation coefficient and percent contribution of input variables are discussed for two pollutants namely, ester and Cd.

Organic Pollutant (Ester)

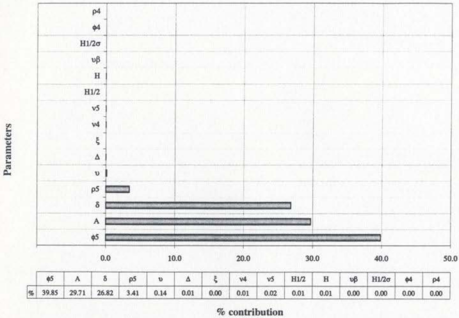
The SA results for ester concentrations in water column and pore water are reported in Table 3.8. The rank correlation coefficients of all input variables are reported. The negative values of rank correlation coefficient (ρ_r) represents an inverse relationship with the output.

Table 3.8. Sensitivity analysis (SA) of ester using rank correlation coefficient (ρ_r)

Parameters	C_w	C_{pw}
φ_5	-0.62	0.00
A	-0.53	0.01
δ	-0.51	0.02
ρ_5	-0.18	0.00
u	0.04	-0.02
Δ	-0.01	-0.78
ξ	0.00	-0.03
v_4	-0.01	0.12
v_5	0.01	0.00
$H_{1/2}$	-0.01	-0.01
H	-0.01	0.00
υ_B	0.00	0.00
$H_{1/2\sigma}$	0.00	0.37
ϕ_4	0.00	-0.34
ρ_4	-0.01	-0.25

For ester concentrations in the water column C_w, the organic content of *SS* (ϕ_5) has the highest rank correlation coefficient of -0.62. The other key input variables are A and δ. The corresponding rank correlation coefficient values are -0.53 and -0.51, respectively. This implies that an increase in organic content and size of *SS* will result in decrease in the ester concentration in the water column. The higher organic fraction captures pollutants from the water column and settles down. This implies that the deposition process is the most important process in decreasing pollutant concentration in the water column. The remaining input parameters do not significantly affect the water column concentration. Figure 3.13 is a tornado graph for representing percent contribution of each input variable. The three input parameters (ϕ_5, A and δ) contribute more than 96% of the total variance of the water column concentration and the remaining variables contribute less than 4%.

The key input variables for pore water concentration are sediment depth (Δ), half-life in sediments ($H_{1/2d}$), density (ρ_4), and organic fraction (ϕ_4) of sediments (Table 3.8). The thickness of the sediment layer (Δ) inversely affects the pore water concentration. It contributes more than 60% of the total variance of pore water concentration. The longer half-life in sediment provides more time for organic pollutants to leach into pore water from the sediment. The organic fraction (12%) and density (7%) of sediments also contribute significantly to the pore water concentration (Figure 3.14).



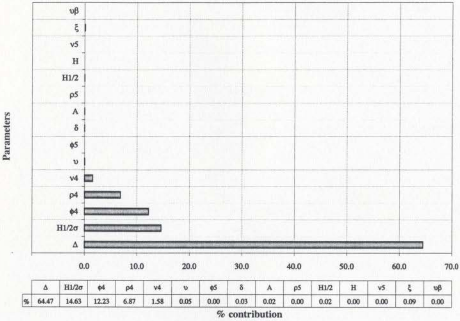
	ϕ5	A	δ	ρ5	υ	Δ	ξ	ν4	ν5	H1/2	H	υβ	H1/2σ	ϕ4	ρ4
%	39.85	29.71	26.82	3.41	0.14	0.01	0.00	0.01	0.02	0.01	0.01	0.00	0.00	0.00	0.00

Figure 3.13. Percent contribution of input variables to ester water column concentration

Heavy Metals (Cd)

Sensitivity analysis results of the aquivalence based model for Cd is presented in Table 3.9. The sensitivity of the output concentrations (C_W and C_{PW}) is measured with the help of the rank correlation coefficient and by determining the percent contribution of input variables. The key input variables for water column concentration are the partitioning coefficients of Cd for sediment (K_σ) and *SS* (K_π). The other important parameter is advective velocity (u).

The advective velocity affects water column concentration in two ways; the flushing of water from the control volume negatively affects the water column concentration; at the same time it can also scour the deposited material to increase the resuspension, which results in an increase in concentration, which is a positive effect. Overall it has a positive effect on C_W. The partitioning coefficients and velocity contribute to more than 90% of the variance in the water column concentration (Figure 3.15).



	Δ	H1/2σ	ϕ4	ρ4	v4	υ	ϕ5	δ	A	ρ5	H1/2	H	v5	ξ	υβ
%	64.47	14.63	12.23	6.87	1.58	0.05	0.00	0.03	0.02	0.00	0.02	0.00	0.00	0.09	0.00

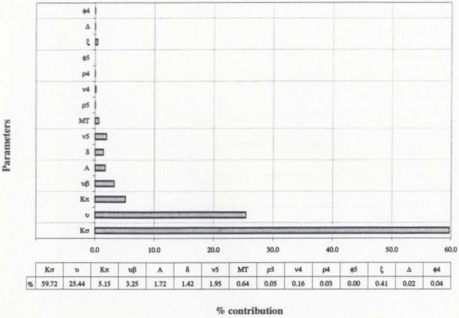
Figure 3.14. Percent contribution of input variables to ester pore water concentration

The Cd pore water concentration (C_{PW}) is mainly affected by the partitioning coefficient of sediment (K_σ). The pore water concentration is highly sensitive to K_σ as it contributes more than 95% to the overall variance (Figure 3.16). The inverse effect of K_σ does not allow heavy metal to leach into the pore water.

Table 3.9. Sensitivity analysis (SA) of Cd using rank correlation coefficient (ρ_r)

Parameters	C_w	C_{PW}
K_σ	-0.69	-0.98
u	0.45	-0.02
K_τ	-0.20	0.00
υ_B	-0.16	-0.16
A	-0.12	0.01
δ	-0.11	0.01
v_s	0.12	0.01
MT	0.07	-0.01
ρ_s	-0.02	0.01
v_d	0.04	0.03
ρ_d	0.02	0.01
φ_s	0.00	0.00
ξ	0.06	0.01
Δ	0.01	0.01
φ_d	-0.02	-0.02

The SA results are presented for ester and Cd concentrations in the water column and pore water. The intention here is to identify and highlight the key input parameters and processes that determine the fate of contaminants in the marine environment. The results of SA show that in the case of organic pollutants, the water column concentration is mainly affected by the deposition process. The organic pore water concentration is mainly affected by half-life ($H_{1/2d}$) in sediments, density (ρ_d), organic content (φ_d) and depth (Δ) of sediments. The fate of heavy metals in the water column and pore water (K_σ and K_τ) is a function of partitioning coefficients and advective velocity (u).



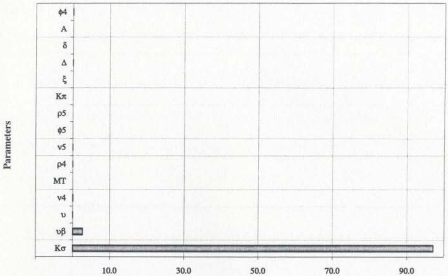
	Kσ	υ	Kπ	υβ	A	δ	v5	MT	ρ5	v4	ρ4	φ5	ξ	Δ	φ4
%	59.72	25.44	5.15	3.25	1.72	1.42	1.95	0.64	0.05	0.16	0.03	0.00	0.41	0.02	0.04

Figure 3.15. Percent contribution of input variables to Cd water column concentration

3.4. MODEL OUTPUT

3.4.1. LOGNORMAL DISTRIBUTION

The concentration of pollutants in environmental media generally follows a positive skewed distribution with a long tail to the right (Sadiq, 1997; Standard Methods, 1998). The environmental concentrations may vary by orders of magnitude and wide variation is observed. The fugacity/aquivalence model outputs; C_W and C_{PW} for ester and Cd are shown in Figures 3.7 to 3.12. The MC simulations show that concentrations in both media vary over a wide range and mean values are more than the median for all cases. The major reason for right hand long tail and positive skew in concentration outputs is that fugacity/aquivalence based models are of multiplicative type, which leads to a lognormal (LN) distribution.



	Kσ	υβ	υ	v4	MT	ρ4	v5	ϕ5	ρ5	Kπ	ξ	Δ	δ	A	ϕ4
%	97.08	2.69	0.03	0.09	0.01	0.02	0.02	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.04

Figure 3.16. Percent contribution of input variables to Cd pore water concentration

Burmaster and Hull (1996) described the importance of the two-parameter lognormal distribution in human and ecological risk assessment. They have reasoned that the lognormal distribution is commonly observed in contaminant fate modeling due to the following:

- Many physical, chemical, biological, and toxicological processes tend to create random variables that follow lognormal distribution (Hattis and Burmaster, 1994).

- The mathematical process of multiplying a series of random variables will produce a new random variable, which tends to be lognormal in character (Benjamin and Cornell, 1970).

- Lognormal distributions are self-replicating i.e., products and divisions of lognormal distributions are also lognormal (Crow and Shimizu, 1988).

The above three reasons for obtaining positive skewed distributions are also applicable to contaminant fate modeling outputs in our case as well. Figures 3.17 and 3.18 are lognormal distribution fits to the fugacity model outputs: C_W and C_{PW} for the first simulation trial for ester. The Figure 3.17 represents an empirical distribution function (EDF) of water column concentration estimated from MC simulations, and the fitted lognormal cumulative distribution function (CDF). The lognormal distribution (LN) is defined by 2 parameters: the arithmetic mean (μ_X) and the standard deviation (σ_X) as shown in Figure 3.17.

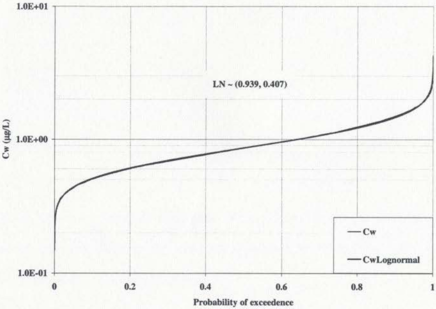


Figure 3.17. An EDF of ester water column concentration estimated from the fugacity based model and fitted lognormal distribution (LN)

Figure 3.18 represents an EDF of ester pore water concentration, which is the second output of MC simulations using the fugacity based model. The fitted lognormal cumulative distribution function (CDF) is also shown. In both cases a good agreement between simulation results and fitted distributions can be observed.

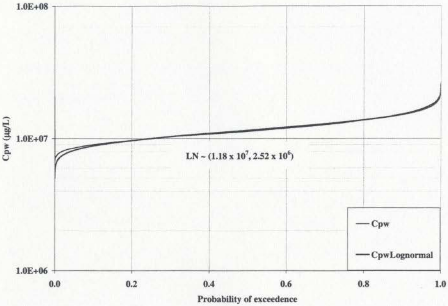


Figure 3.18. An EDF of ester pore water concentration estimated from the fugacity based model and fitted lognormal distribution (LN)

The two-parameter lognormal distribution takes its name from its fundamental property that the logarithm of the random variable is distributed according to normal or Gaussian distribution (Burmaster and Hull, 1996).

$$\{\ln(C)\} \sim N(\mu_Y, \sigma_Y) \qquad (3.2)$$

where.

μ_Y = mean of log of concentration

σ_Y = standard deviation of log of concentration

C = lognormally distributed concentration

The @Risk (Palisade, 1997) uses the arithmetic mean (μ_X) and standard deviation (σ_X) of concentration data to generate the lognormal distribution (e.g., Figures 3.17 and 3.18). The arithmetic mean (μ_X) and standard deviation (σ_X) are related to μ_Y and σ_Y by the following relationships

$$\mu_Y = ln\left[\frac{\mu_X^2}{\sqrt{\sigma_X^2 + \mu_X^2}}\right] \tag{3.3}$$

and

$$\sigma_Y = \sqrt{ln\left[\frac{\sigma_X^2 + \mu_X^2}{\mu_X^2}\right]} \tag{3.4}$$

The (100 × p)th percentile value for the underlying normal distribution can be calculated as :

$$\begin{aligned} \{ln[C]\}_p &= \{N \sim (\mu_Y, \sigma_Y)\}_p \\ &= \mu_Y + z(p) \times \sigma_Y \end{aligned} \tag{3.5}$$

Therefore by extension, the $(100 \times p)^{th}$ percentile for a lognormal distribution can be calculated as follows:

$$
\begin{aligned}
[C]_p &= [exp[N \sim (\mu_Y, \sigma_Y)]]_p \\
&= exp[\mu_Y + z(p) \times \sigma_Y]
\end{aligned}
\tag{3.6}
$$

where,

$z(p) = \Phi^{-1}(Y)$ = inverse of cumulative distribution function

μ_Y = arithmetic mean of concentration (water column or pore water)

σ_Y = standard deviation of concentration

$[C]_p$ = Pollutant concentration in any media at desired percentile level (p)

Generally, mean, median, 90th or 95th percentiles are used as representative environmental concentrations. The U.S. EPA (2000a) used the average value for defining representative environmental concentration. Lenwood et al. (1998) have proposed the 90th percentile of concentration as the representative environmental concentration of heavy metals as an exposure to the fresh water community. In this research, a conservative approach was adopted and the 95th percentile is defined as the representative estimate of the environmental concentration. This concentration is called the predicted environmental concentration (*PEC*) in the CHARM model (Thatcher et al., 1999).

For $p = 0.95 \quad \Rightarrow \qquad z(p) = 1.645$

Therefore, equation 3.6 becomes

$$C_{0.95} = exp[\,\mu_Y + 1.645 \times \sigma_Y\,] \tag{3.7}$$

where, $C_{0.95}$ is the representative concentration in the media. Substituting equations 3.3 and 3.4 in equation 3.7 will give

$$C_{w,0.95} = exp\left[ln\left(\frac{\mu_w^2}{\sqrt{\sigma_w^2 + \mu_w^2}}\right) + 1.645 \times \sqrt{ln\left(\frac{\sigma_w^2 + \mu_w^2}{\mu_w^2}\right)}\right] \tag{3.8}$$

Similarly,

$$C_{pw,0.95} = exp\left[ln\left(\frac{\mu_{pw}^2}{\sqrt{\sigma_{pw}^2 + \mu_{pw}^2}}\right) + 1.645 \times \sqrt{ln\left(\frac{\sigma_{pw}^2 + \mu_{pw}^2}{\mu_{pw}^2}\right)}\right] \tag{3.9}$$

where,

$C_{w,0.95}$ = pollutant water column concentration at 95th percentile ($p = 0.95$)

$C_{pw,0.95}$ = pollutant pore water concentration at 95th percentile ($p = 0.95$)

μ_w = arithmetic mean of lognormally distributed water column concentration

σ_w = standard deviation of lognormally distributed water column concentration

μ_{pw} = arithmetic mean of lognormally distributed pore water concentration

σ_{pw} = standard deviation of lognormally distributed pore water concentration

Equations 3.8 and 3.9 can be used to determine the water column and pore water concentrations at the 95th percentile while knowing the mean and standard deviation of the underlying lognormal distribution.

3.4.2 OUTPUT CONCENTRATION RESULTS

The fugacity or aquivalence (f_2 and/or A_2) determines the concentration of pollutants in the water column and pore water, respectively. The f_2 and A_2 are functions of D-values, which further linearly relate to impact area (A_w). The impact area is assumed to be circular, which is a function of the square of the radius. Therefore, f_2 (and A_2) may be inversely proportional to the square of the impact radius (R). The f_2 (and A_2) are linear functions of loading rates (E_2 and E_4). Therefore f_2 (and A_2) increases linearly with an increase in total pollutant loading.

Tables 3.10 and 3.11 summarize the mean (μ_w) and standard deviation (σ_w) of concentration in the water column, respectively, for the pollutants under study. The results of 15 simulation data sets are summarized in these tables. The comparison of average ester concentration in the water column (μ_w) for trials 1 and 2 shows that with an increase in the impact area, the concentration decreases (Table 3.10). By increasing the impact radius from 50 m to 100 m, the mean concentration is decreased from 0.94 to 0.24 μg/L for a 150 kg/hr loading rate. The concentration further decreases to 0.01 μg/L approximately for a 500 m impact radius. The mean concentration decreases proportionally with an increase in the square of the radius. A similar effect can also be observed by comparing trials 6 and 7 or 11 and 12.

Since lognormal distribution is a skewed distribution, the standard deviation (σ_w) may not necessarily follow the trend observed for mean values. The comparison of standard deviation of ester concentration in the water column (σ_w) for trials 1 and 2 shows that by increasing the impact radius from 50 m to 100 m, the σ_w is decreased from 0.41 to 0.10 for the 150 kg/hr loading rate (Table 3.12). The σ_w further decreases to 0.004 μg/L approximately for the 500 m impact radius. A similar effect can also be observed by comparing trials 6 and 7 or 11 and 12.

The comparison of trial 1 and 6 for ester shows that average concentration decreases from 0.94 to 0.47 μg/L when pollutant loading is reduced from 150 kg/hr to 75 kg/hr. It is further reduced to 0.03 μg/L for 5 kg/hr (Trial 11). This shows an approximately linear relationship between loading rate and concentration in the water column. The comparison of trials 1 and 6 for ester shows that the standard deviation of concentration decreases from 0.41 to 0.20 μg/L when pollutant loading is reduced from 150 kg/hr to 75 kg/hr. It is further reduced to 0.013 μg/L for 5 kg/hr (Trial 11).

A similar trend can be seen for other pollutants listed in Table 3.10 and 3.11. Figures 3.19 and 3.20 are the 3D surface plots of the mean (μ_{pw}) and standard deviation (σ_{pw}) of water column concentrations for ester as a function of pollutant loading rates (E) and impact radius (R).

Tables 3.12 and 3.13 summarize the mean (μ_{pw}) and standard deviation (σ_{pw}) of pore water concentrations, respectively for various pollutants. The results of 15 simulation data sets are summarized. The comparison of ester concentration in pore water for trials 1 and 2 shows that with an increase in the impact area, the concentration decreases. For impact radii of 50 m to 100 m the average concentration is decreased from 11.8 to 2.96 g/L for the 150 kg/hr loading rate (Table 3.12). The concentration further decreases to 0.12 g/L at 500 m impact radius. The average concentration decreases proportionally with an increase in square of the impact radius. A similar effect of impact radius can also be observed by comparing trials 6 and 7 or 11 and 12.

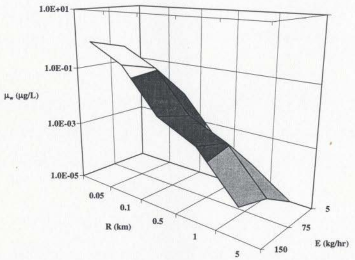


Figure 3.19. A 3-D surface plot of mean water column concentration (μ_w) of ester as a function of loading rate and impact radius

The comparison of the standard deviation of ester concentration in the water column (σ_{pw}) for trials 1 and 2, shows that by increasing the impact radius from 50 m to 100 m, the (σ_{pw}) is decreased from 2.52 to 0.63 g/L for the 150 kg/hr loading rate (Table 3.13).

The σ_{pw} further decreases to 0.025 g/L approximately at the 500 m impact radius. A similar effect can also be observed by comparing trials 6 and 7 or 11 and 12.

The comparison of trials 1 and 6 for ester shows that mean pore water concentration (μ_{pw}) decreases from 11.8 to 5.91 g/L when pollutant loading is reduced from 150 kg/hr to 75 kg/hr. It is further reduced to 0.39 µg/L for 5 kg/hr (Trial 11). This implies an approximately linear relationship between loading rate and concentration in pore water. The comparison of trial 1 and 6 for ester shows that the standard deviation of pore water concentration decreases from 2.52 to 1.25 g/L when pollutant loading is reduced from 150 kg/hr to 75 kg/hr. It is further reduced to 0.084 µg/L for 5 kg/hr (Trial 11).

A similar trend can be seen for other pollutants listed in Tables 3.12 and 3.13. Figures 3.21 and 3.22 are the 3D surface plots of the mean and standard deviation of pore water concentration for ester as a function of pollutant loading rate and impact radius.

The results of MC simulations are summarized in Tables 3.10 to 3.13. The results are provided in the form of mean and standard deviation of 10,000 iterations for each simulation. As the mean and standard deviation are the characteristic parameters of the lognormal distribution, the parameters of the lognormal distribution can be used to predict representative environmental concentration in the water column and pore water at any desired percentile level. In the next section these characteristic parameters are used to develop regression models for each pollutant in terms of impact radius and pollutant loading rates.

Table 3.10. The results of MC simulations for mean (μ_w) water column concentration (µg/L)

Trials	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Naphthalene	Ester
1	7.75E-05	6.77E-05	1.11E-04	3.11E-05	6.58E-08	3.12E-05	3.12E-05	1.44E-04	1.22E-11	9.40E-01
2	2.09E-05	1.85E-05	2.95E-05	8.20E-06	1.66E-08	8.00E-06	8.00E-06	3.67E-05	3.06E-12	2.35E-01
3	9.65E-07	7.85E-07	1.26E-06	3.39E-07	6.59E-10	3.50E-07	3.50E-07	1.62E-06	1.23E-13	9.45E-03
4	2.52E-07	2.06E-07	3.24E-07	8.92E-08	1.65E-10	8.77E-08	8.77E-08	4.20E-07	3.07E-14	2.36E-03
5	1.02E-08	8.32E-09	1.34E-08	3.51E-09	6.63E-12	3.50E-09	3.50E-09	1.71E-08	1.23E-15	9.43E-05
6	2.53E-05	2.34E-05	3.64E-05	1.04E-05	2.20E-08	1.00E-05	1.00E-05	4.66E-05	4.08E-12	4.69E-01
7	6.99E-06	6.27E-06	9.58E-06	2.70E-06	5.52E-09	2.62E-06	2.62E-06	1.26E-05	1.02E-12	1.18E-01
8	3.13E-07	2.62E-07	4.07E-07	1.16E-07	2.23E-10	1.13E-07	1.13E-07	5.33E-07	4.09E-14	4.71E-03
9	8.46E-08	6.70E-08	1.03E-07	2.86E-08	5.54E-11	2.91E-08	2.91E-08	1.37E-07	1.02E-14	1.18E-03
10	3.55E-09	2.67E-09	4.23E-09	1.20E-09	2.16E-12	1.17E-09	1.17E-09	5.39E-09	4.10E-16	4.71E-05
11	6.23E-07	5.69E-07	9.23E-07	2.57E-07	5.54E-10	2.58E-07	2.58E-07	1.20E-06	1.02E-13	3.12E-02
12	1.76E-07	1.53E-07	2.39E-07	6.80E-08	1.36E-10	6.86E-08	6.86E-08	3.17E-07	2.56E-14	7.85E-03
13	8.18E-09	6.52E-09	1.07E-08	2.83E-09	5.50E-12	2.80E-09	2.80E-09	1.33E-08	1.02E-15	3.15E-04
14	2.03E-09	1.63E-09	2.55E-09	7.27E-10	1.38E-12	7.21E-10	7.21E-10	3.53E-09	2.56E-16	7.86E-05
15	8.58E-11	6.50E-11	1.08E-10	2.98E-11	5.46E-14	2.87E-11	2.87E-11	1.37E-10	1.02E-17	3.14E-06

Table 3.11. The results of MC simulations for standard deviation (σ_w) of water column concentration (µg/L)

Trials	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Naphthalene	Ester
1	1.54E-04	1.64E-04	3.23E-04	7.61E-05	1.32E-07	7.72E-05	7.72E-05	3.79E-04	6.66E-12	4.07E-01
2	4.25E-05	5.01E-05	9.69E-05	2.08E-05	3.36E-08	2.15E-05	2.15E-05	1.03E-04	1.68E-12	1.00E-01
3	2.58E-06	2.24E-06	4.87E-06	1.01E-06	1.20E-09	1.03E-06	1.03E-06	6.05E-06	6.79E-14	4.09E-03
4	7.34E-07	6.12E-07	1.50E-06	2.62E-07	3.13E-10	2.71E-07	2.71E-07	1.61E-06	1.73E-14	1.02E-03
5	3.42E-08	2.54E-08	6.18E-08	1.05E-08	1.23E-11	1.02E-08	1.02E-08	7.78E-08	6.82E-16	4.01E-05
6	4.58E-05	6.06E-05	1.08E-04	2.62E-05	4.25E-08	2.47E-05	2.47E-05	1.19E-04	2.32E-12	1.98E-01
7	1.48E-05	1.76E-05	3.09E-05	6.80E-06	1.06E-08	6.41E-06	6.41E-06	3.73E-05	5.56E-13	5.03E-02
8	7.94E-07	7.61E-07	1.51E-06	3.47E-07	5.21E-10	3.20E-07	3.20E-07	1.88E-06	2.31E-14	2.01E-03
9	2.55E-07	1.95E-07	3.69E-07	8.36E-08	1.24E-10	8.63E-08	8.63E-08	4.80E-07	5.61E-15	5.07E-04
10	1.26E-08	7.74E-09	1.84E-08	4.32E-09	3.88E-12	3.83E-09	3.83E-09	1.85E-08	2.40E-16	2.02E-05
11	1.07E-06	1.38E-06	2.71E-06	6.24E-07	1.03E-09	6.52E-07	6.52E-07	3.18E-06	5.90E-14	1.31E-02
12	3.53E-07	4.13E-07	7.68E-07	1.75E-07	2.67E-10	1.77E-07	1.77E-07	9.51E-07	1.56E-14	3.38E-03
13	2.21E-08	1.93E-08	4.03E-08	7.80E-09	1.11E-11	7.96E-09	7.96E-09	4.44E-08	6.03E-16	1.36E-04
14	5.97E-09	4.48E-09	9.46E-09	2.07E-09	2.67E-12	2.28E-09	2.28E-09	1.54E-08	1.49E-16	3.38E-05
15	2.70E-10	1.94E-10	5.12E-10	9.36E-11	9.56E-14	8.26E-11	8.26E-11	5.68E-10	5.96E-18	1.35E-06

Table 3.12. The results of MC simulations for mean (μ_{pw}) pore water concentration (μg/L)

Trials	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Naphthalene	Ester
1	2.73E+05	9.64E+05	2.61E+05	4.30E+05	3.09E+00	4.37E+05	4.37E+05	8.53E+05	7.39E-04	1.18E+07
2	6.90E+04	2.54E+05	6.55E+04	1.09E+05	7.72E-01	1.10E+05	1.10E+05	2.13E+05	1.85E-04	2.96E+06
3	2.81E+03	1.05E+04	2.60E+03	4.48E+03	3.08E-02	4.62E+03	4.62E+03	8.51E+03	7.41E-06	1.19E+05
4	7.08E+02	2.64E+03	6.50E+02	1.15E+03	7.70E-03	1.12E+03	1.12E+03	2.12E+03	1.85E-06	2.96E+04
5	2.85E+01	1.08E+02	2.59E+01	4.54E+01	3.13E-04	4.61E+01	4.61E+01	8.67E+01	7.42E-08	1.19E+03
6	9.09E+04	3.26E+05	8.62E+04	1.44E+05	1.04E+00	1.44E+05	1.44E+05	2.85E+05	2.46E-04	5.91E+06
7	2.29E+04	8.60E+04	2.16E+04	3.72E+04	2.58E-01	3.63E+04	3.63E+04	7.12E+04	6.18E-05	1.48E+06
8	9.44E+02	3.55E+03	8.76E+02	1.51E+03	1.03E-02	1.50E+03	1.50E+03	2.87E+03	2.47E-06	5.93E+04
9	2.36E+02	8.80E+02	2.20E+02	3.74E+02	2.58E-03	3.78E+02	3.78E+02	7.24E+02	6.17E-07	1.48E+04
10	9.48E+00	3.47E+01	8.64E+00	1.51E+01	1.04E-04	1.53E+01	1.53E+01	2.88E+01	2.47E-08	5.93E+02
11	2.28E+03	8.02E+03	2.18E+03	3.61E+03	2.57E-02	3.61E+03	3.61E+03	7.04E+03	6.16E-06	3.94E+05
12	5.76E+02	2.13E+03	5.40E+02	9.24E+02	6.44E-03	9.31E+02	9.31E+02	1.81E+03	1.55E-06	9.86E+04
13	2.35E+01	8.81E+01	2.17E+01	3.74E+01	2.60E-04	3.72E+01	3.72E+01	7.20E+01	6.17E-08	3.95E+03
14	5.90E+00	2.18E+01	5.49E+00	9.37E+00	6.51E-05	9.29E+00	9.29E+00	1.79E+01	1.54E-08	9.88E+02
15	2.36E-01	9.10E-01	2.17E-01	3.75E-01	2.61E-06	3.74E-01	3.74E-01	7.03E-01	6.18E-10	3.95E+01

Table 3.13. The results of MC simulations for standard deviation (σ_{pw}) of pore water concentration (µg/L)

Trials	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Naphthalene	Ester
1	3.28E+05	2.64E+06	8.28E+05	1.30E+06	4.27E+00	1.31E+06	1.31E+06	2.46E+06	2.92E-04	2.52E+06
2	8.24E+04	7.22E+05	2.05E+05	3.28E+05	1.07E+00	3.28E+05	3.28E+05	6.08E+05	7.29E-05	6.32E+05
3	3.40E+03	3.03E+04	8.17E+03	1.39E+04	4.25E-02	1.46E+04	1.46E+04	2.41E+04	2.95E-06	2.53E+04
4	8.67E+02	7.65E+03	2.03E+03	3.53E+03	1.06E-02	3.42E+03	3.42E+03	5.93E+03	7.35E-07	6.33E+03
5	3.51E+01	3.19E+02	8.13E+01	1.38E+02	4.36E-04	1.45E+02	1.45E+02	2.51E+02	2.94E-08	2.52E+02
6	1.09E+05	8.98E+05	2.73E+05	4.38E+05	1.46E+00	4.33E+05	4.33E+05	8.29E+05	9.78E-05	1.25E+06
7	2.74E+04	2.46E+05	6.74E+04	1.14E+05	3.57E-01	1.08E+05	1.08E+05	2.03E+05	2.50E-05	3.16E+05
8	1.15E+03	1.05E+04	2.77E+03	4.66E+03	1.43E-02	4.63E+03	4.63E+03	8.19E+03	9.87E-07	1.27E+04
9	2.85E+02	2.58E+03	6.98E+02	1.14E+03	3.57E-03	1.15E+03	1.15E+03	2.10E+03	2.44E-07	3.17E+03
10	1.15E+01	9.95E+01	2.69E+01	4.60E+01	1.44E-04	4.82E+01	4.82E+01	8.23E+01	9.79E-09	1.27E+02
11	2.74E+03	2.20E+04	6.92E+03	1.08E+04	3.53E-02	1.08E+04	1.08E+04	2.00E+04	2.44E-06	8.42E+04
12	6.96E+02	6.13E+03	1.70E+03	2.81E+03	8.90E-03	2.84E+03	2.84E+03	5.23E+03	6.25E-07	2.10E+04
13	2.83E+01	2.56E+02	6.79E+01	1.17E+02	3.64E-04	1.15E+02	1.15E+02	2.07E+02	2.44E-08	8.42E+02
14	7.18E+00	6.30E+01	1.75E+01	2.84E+01	9.05E-05	2.86E+01	2.86E+01	5.12E+01	6.17E-09	2.11E+02
15	2.86E-01	2.73E+00	6.76E-01	1.15E+00	3.67E-06	1.15E+00	1.15E+00	1.98E+00	2.44E-10	8.36E+00

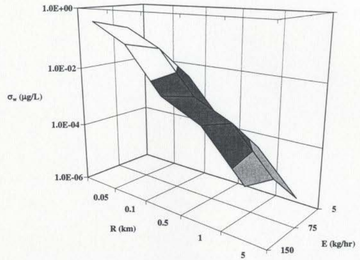


Figure 3.20. A 3-D surface plot of standard deviation of the water column concentration (σ_w) of ester as a function of loading rate and impact radius

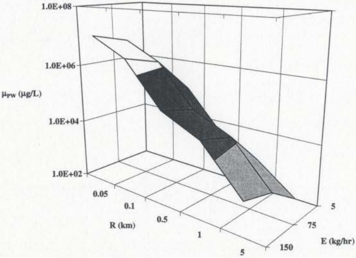


Figure 3.21. A 3-D surface plot of the mean pore water concentration (μ_{pw}) of ester as a function of loading rate and impact radius

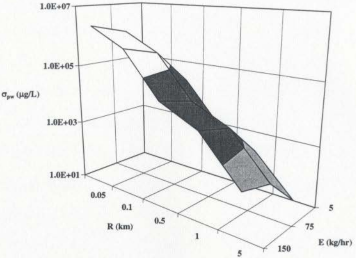


Figure 3.22. A 3-D surface plot of the standard deviation of pore water concentration (σ_{pw}) of ester as a function of loading rate and impact radius

3.5. REGRESSION MODELS

The immediate objective is to develop a relationship for environmental concentration (equations 3.8 and 3.9) as a function of loading rate and impact radius. The characteristic parameters of the lognormal distribution are the mean and standard deviation, which are estimated from MC simulations. They are used to estimate predicted environmental concentration (*PEC*). The environmental concentration can be expressed in terms of pollutant loading rate (*E*) and impact radius (*R*).

A similar approach is adopted at Louisiana Bay for the discharges of produced waters. The CORMIX model is used to estimate the dilution factors (*DF*) available at known distances from the point of discharge. Under site specific conditions, the dilution factor

(*DF*) is calculated as a function of discharge rate (*G*) (Meinhold et al., 1995) at known distances using regression analysis.

Regression methods are frequently used to analyze data from unplanned experiments and are also very useful in the design of experiments. The control or independent variables are varied to observe the effects of these factors on the output of the model. The multiple regression models involve more than one variable. The general form for fitting multiple linear regression is given as

$$\hat{Z}=\alpha_0+\alpha_1 X_1+\alpha_2 X_2+\alpha_3 X_3+\cdots\cdots+\alpha_k X_k+\varepsilon \qquad (3.10)$$

where X_1, X_2 ...... X_k are the independent or control variables, the unknown parameters "α's" are regression coefficients and "ε" is an error term. The method of least squares is generally used to estimate the regression coefficients.

In multiple linear regression, the relationship between variables is assumed to be linear. In practice this assumption can virtually never be confirmed; fortunately, multiple regression procedures are not greatly affected by minor deviations from this assumption. Transformation of data is generally performed to convert into a linear form. Linear regression assumes that the scatter of the points around the line follows a Gaussian distribution and that the standard deviation is the same at all values of independent variables (*Xs*).

The MC simulation results show that the concentrations in multimedia are a function of pollutant loading and impact radius under given conditions that can also be determined from the physics of the processes. When allowing for any type of relationship between the independent variables and the dependent variable, two issues arise - First, what types of relationships are logical, that is, are they interpretable in a meaningful manner. The second issue is how to compute this relationship. The fugacity (f_2) or aquivalence (A_2) of water is a linear function of pollutant loading rate (E) and area of impact (A_w). From a general observation of the data in Tables 3.10 to 3.13, a decrease in concentration is observed with a decrease in pollutant loading and an increase in impact radius. A multiplicative regression model form can be anticipated.

$$C_i \sim f\left(E \times \frac{1}{R}\right) \tag{3.11}$$

The transformation of data is very common in regression analysis. The log transformation is the most common type of transformation. The log transformation of concentration (*LC*), pollutant loading rates (*LE*) and impact radius (*LR*) can convert the above relationship into a linear form, which is similar to equation 3.10.

$$LC = a + b \times LE + c \times LR \tag{3.12}$$

where a, b and c are regression coefficients and can be calculated by multiple linear regression. The objective of fitting a best linear model is achieved through minimizing the sum-of-squares (SS_i) of the vertical distances of the point from the predicted line. The most common technique employed to estimate the parameters in linear models is the method of least squares and the best estimates of the parameters are obtained by using

$$min\, SS_i = min \sum (Le_i)^2 = min \sum (LC_i - \hat{LC}_i)^2 \tag{3.13}$$

where the $min\ SS_i$ represents a minimum sum of squares of the errors. Le_i represents the i^{th} term of errors. LC_i is the i^{th} term of simulated values and the $\hat{LC}_i$ is the i^{th} value determined from the model equations (Pai et. al. 2000).

After estimating the regression parameters, an essential aspect of the analysis is to test the appropriateness of the overall model. There are several parameters to evaluate the appropriateness of a model. The ratio of the regression sum of squares to the total sum of squares (SS_R/SS_T) explains the proportion of variance accounted for in the dependent variable (LC) by the model. This ratio is equivalent to the coefficient of determination (R^2) that has a value between 0 and 1. Even when the dependent variable is not normally distributed, this measure may help evaluate how well the model fits the data. The plot of observed and predicted values also gives an indication of the appropriateness of the model. If the model is appropriate for the data, then the points roughly follow a straight line. The normal probability plot of residuals will give an indication of whether or not the residuals (errors) are normally distributed. This plot is used to check the basic assumption behind the method of least squares.

3.5.1. DEVELOPMENT OF REGRESSION MODELS

In this section, a methodology for development of empirical models is given for the mean (μ_{pw}) and standard deviation (σ_{pw}) of ester pore water concentration. The Minitab software (version 12.1) was used for the multiple regression (Minitab, 1998). The mean concentration (μ_{pw}), loading rate and impact radius data were first log transformed and multiple regression was performed (Table 3.10). The following equations were obtained for the mean (μ_{pw}) and standard deviation (σ_{pw})

$$\hat{LC}_{\mu} = 2.296 - 1.999\ LR + 1.000\ LE \tag{3.14}$$

where,

$a1 = (2.296, 0.003)$

$b1 = (1.000, 0.002)$

$c1 = (1.999, 0.0001)$

$\hat{LC}_{\mu}$ = an estimated value of μ_{pw} (or LC_{μ}) from regression model

Similarly,

$$\hat{LC}_{\sigma} = 1.625 - 2.000\ LR + 1.001\ LE \tag{3.15}$$

where,

$a2 = (1.625, 0.002)$

$b2 = (1.001, 0.001)$

$c2 = (2.000, 0.001)$

$\dot{LC}_{\sigma}$ = an estimated value of σ_{pw} (or LC_{σ}) from regression model

Table 3.14 provides the regression statistics of the above models. By comparing equations 3.14 and 3.15 with equation 3.12, the coefficients (a, b and c) can be estimated. The uncertainty in the coefficient is estimated by the standard deviation of the estimate (SE). The SE values are very low in comparison to the estimates and coefficients are highly significant i.e., $p < 0.0001$. The errors or residuals in the regression are defined by $Le_i = LC_i - \dot{LC}_i$. The normality of residuals is also checked for both models as shown in Figures 3.23 and 3.24. No serious deviation from assumptions is observed.

Table 3.14. Statistics of regression models for mean and standard deviation of ester pore water concentration

Log transformed regression statistics						Bias correction (B)	Predictor actual value
Parameter	Predictor	Coefficient	SE	t	$p > t$		
Mean μ_{pw}	$a1$	2.296	3.0E-04	9019	0.000	1.0000003	197.70
	$b1$	1.000	2.0E-04	6837	0.000		1.00
	$c1$	-1.999	1.3E-04	-15309	0.000		-2.00
St. dev. σ_{pw}	$a2$	1.623	1.3E-03	1284	0.000	1.000007	41.98
	$b2$	1.001	1.0E-03	1377	0.000		1.00
	$c2$	-2.000	1.0E-03	-3083	0.000		-2.00

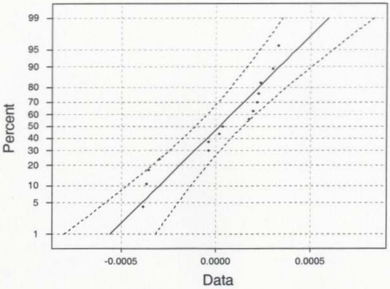


Figure 3.23. Normal probability plot of residuals for mean ester pore water concentration

The residuals were also plotted against the log of predicted concentration in Figure 3.25. This plot is used to observe the patterns that could suggest serious deviation from assumption of constant variance, error in analysis or model inadequacy (Dingman and Sharma, 1997).

Regression that predicts the logarithm of a quantity usually gives low biased predictions of the anti-logarithm, which is the actual model (Dingman and Sharma, 1997). A correction is used for this bias by multiplying the real space predictions by a robust bias-correction factor (B).

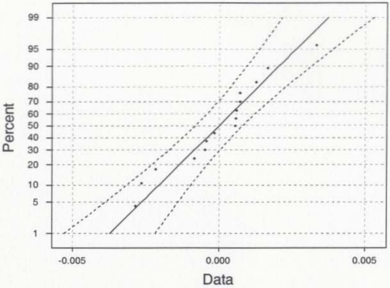


Figure 3.24. Normal probability plot of residuals for standard deviation of ester pore water concentration

$$B = \frac{\Sigma 10^{Le_i}}{N} \tag{3.16}$$

where, *N* are the number of data points. The bias correction factors (*B*) are very low for both models, i.e., 1.0000003 and 1.000007 for mean and standard deviation models, respectively. By applying the correction and taking anti-logarithms of equations 3.14 and 3.15, the following relationships can be obtained.

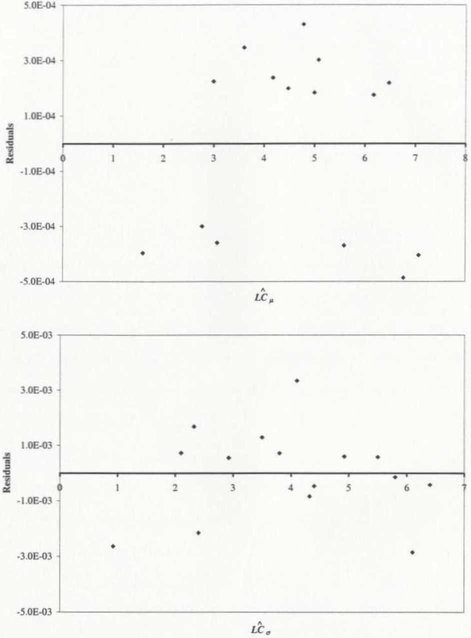


Figure 3.25. Model residuals scatter plot for ester pore water concentration

$$C_{\mu} = 197.70\left(\frac{E^{1.00}}{R^{2.00}}\right) \text{ for mean ester pore water concentration} \tag{3.17}$$

and

$$C_{\sigma} = 41.98\left(\frac{E^{1.00}}{R^{2.00}}\right) \text{ for standard deviation of ester pore water concentration} \tag{3.18}$$

The model appropriateness can be determined by inspecting the coefficient of determination (R^2) and its adjusted value (R_a^2). The adjusted values of R^2 values for both models are approximately 1, which shows a very good agreement between predicted and simulated values (Table 3.14). The average residual values $E(Le)$ and standard deviation of residuals $S(Le)$ are used for checking accuracy and precision of a model, respectively. Both parameters are grouped into one, by defining $RMSE_{Le}$ (root mean squared error).

$$RMSE_{Le} = \left(E^2(Le) + S^2(Le)\right)^{1/2} \tag{3.19}$$

The $RMSE_{LE}$ are calculated for both models as given in Table 3.15.

Table 3.15. Model appropriateness statistics for regression models

Pollutants	R^2	R_a^2	$RMSE_{Le}$	F	$p > F$
Ester	1.000	1.000	3.61E-04	1.41E+08	0.000
Cd	1.000	1.000	1.79E-03	5.70E+06	0.000

3.5.2. SUMMARY OF REGRESSION MODELS

The regression model development procedure described in the preceding section was applied to all pollutants for water column and pore water individually. A summary of the coefficients for different regression models is given in Tables 3.16 and 3.17.

The R_a^2 value estimated for all models were more than 0.9999 and were rounded off to the third decimal place to make 1.000. The bias correction factors (B) calculated for these models are very small and do not have any significant effect on the final result after transformation. The bias correction factors are not reported in Tables 3.16 and 3.17. The $RMSE_L$ are calculated and reported for all regression models. The smaller values show high accuracy and precision in regression model predictions. The values of regression coefficients and their standard error values are reported to determine the uncertainty in the estimates.

The regression models are developed as a function of loading rate (E) and impact radius (R) which can be used in equations 3.8 and 3.9 to get the predicted environmental concentration at any desired percentile ($p = 0.95$). The mean and standard deviations of the water column (μ_w and σ_w) and pore water (μ_{pw} and σ_{pw}) concentrations are a function of pollutant loading and impact radius. the coefficients are given in Tables 3.16 and 3.17. The final form of the equations 3.8 and 3.9 becomes

Table 3.16. Statistics of regression models for mean and standard deviation water column concentration

Pollutants	μ_w					σ_w				
	*$a1$	$b1$	$c1$	$RMSE_{Lr}$	R^2_a	*$a2$	$b2$	$c2$	$RMSE_{Lr}$	R^2_a
As	(-10.01, 0.02)	(1.002, 0.005)	(1.932, 0.007)	0.01798	1.000	(-9.67, 0.03)	(1.01, 0.011)	(1.798, 0.014)	0.0391	0.999
Cd	(-10.20, 0.02)	(1.005, 0.004)	(1.967, 0.005)	0.01423	1.000	(-9.76, 0.03)	(1.009, 0.009)	(1.932, 0.011)	0.0316	1.000
Cr	(-10.99, 0.01)	(1.003, 0.004)	(1.965, 0.004)	0.01200	1.000	(-10.41, 0.04)	(1.008, 0.010)	(1.871,0.013)	0.036	1.000
Cu	(-10.54, 0.01)	(1.001, 0.003)	(1.971, 0.003)	0.0086	1.000	(-10.09, 0.02)	(1.006, 0.007)	(1.911, 0.009)	0.0238	1.000
Hg	(-13.26, 0.003)	(1.001, 0.001)	(2.001, 0.001)	0.0032	1.000	(-12.99, 0.03)	(1.006, 0.007)	(2.013, 0.013)	0.0370	1.000
Ni	(-10.17, 0.01)	(0.997,0.004)	(1.971, 0.005)	0.0126	1.000	(-9.687, 0.02)	(0.989, 0.007)	(1.941, 0.009)	0.0239	1.000
Pb	(-10.55, 0.01)	(1.001, 0.003)	(1.972, 0.004)	0.0116	1.000	(-10.088, 0.03)	(1.002, 0.009)	(1.925, 0.012)	0.0320	1.000
Zn	(-10.87, 0.02)	(0.999,0.004)	(1.966, 0.005)	0.0139	1.000	(-10.286, 0.06)	(0.994, 0.015)	(1.869, 0.019)	0.0531	0.999
Naphthalene	(-16.99, 0.001)	(0.999,0.001)	(1.999, 0.001)	0.0006	1.000	(-17.20, 0.01)	(0.987, 0.003)	(1.996, 0.004)	0.0097	1.000
Ester	(-4.804,0.001)	(1.000,0.0004)	(1.999, 0.003)	0.0009	1.000	(-5.172, 0.004)	(1.001, 0.002)	(1.998, 0.002)	0.0049	1.000

*The values are log transformed, take antilog to get the actual values

Table 3.17. Statistics of regression models for mean and standard deviation pore water concentration

Pollutants	μ_{pw}					σ_{pw}				
	*$a1$	$b1$	$c1$	$RMSE_{Lr}$	R^2_a	*$a2$	$b2$	$c2$	$RMSE_{Lr}$	R^2_a
As	(-0.629,0.002)	(1.000, 0.001)	(1.991, 0.001)	0.0028	1.000	(-0.546, 0.004)	(1.000, 0.001)	(1.987, 0.002)	0.0047	1.000
Cd	(-0.056, 0.008)	(0.999, 0.003)	(1.981, 0.004)	0.0097	1.000	(0.4104, 0.014)	(0.998, 0.005)	(1.968, 0.006)	0.0171	1.000
Cr	(-1.163, 0.006)	(0.999, 0.001)	(2.000, 0.001)	0.0030	1.000	(-1.163, 0.006)	(0.999, 0.002)	(2.002, 0.002)	0.0060	1.000
Cu	(-0.427, 0.004)	(1.000, 0.002)	(1.991, 0.002)	0.0050	1.000	(0.058, 0.007)	(1.003, 0.026)	(1.988, 0.003)	0.0091	1.000
Hg	(-5.584, 0.002)	(0.999, 0.001)	(1.998, 0.002)	0.0023	1.000	(-5.44, 0.004)	(0.998, 0.002)	(1.997, 0.002)	0.0051	1.000
Ni	(-0.0567 0.008)	(0.999, 0.003)	(1.981, 0.004)	0.010	1.000	(0.409, 0.013)	(0.997, 0.005)	(1.975, 0.006)	0.0158	1.000
Pb	(-0.431, 0.005)	(1.002, 0.002)	(1.990, 0.002)	0.0057	1.000	(0.0574, 0.009)	(1.003, 0.003)	(1.981, 0.004)	0.0108	1.000
Zn	(-1.146, 0.005)	(1.000, 0.001)	(1.999, 0.002)	0.0050	1.000	(-0.692, 0.010)	(1.000, 0.003)	(2.001, 0.003)	0.0091	1.000
Naphthalene	(-9.209, 0.001)	(1.000, 0.001)	(2.000, 0.001)	0.0055	1.000	(-9.608, 0.003)	(0.999, 0.001)	(2.001, 0.001)	0.0038	1.000
Ester	(2.296, 0.0003)	(1.000,0.0002)	(1.999, 0.0001)	0.0004	1.000	(1.625,0.0013)	(1.001, 0.001)	(2.000, 0.001)	0.0018	1.000

*The values are log transformed, take antilog to get the actual values

$$C_{media,0.95} = exp\left[ln\left(\frac{\left(a1\left[\frac{E^{b1}}{R^{c1}} \right] \right)^2}{\sqrt{\left(a2\left[\frac{E^{b2}}{R^{c2}} \right] \right)^2 + \left(a1\left[\frac{E^{b1}}{R^{c1}} \right] \right)^2}} \right) + 1.645 \times \sqrt{ln\left(\frac{\left(a2\left[\frac{E^{b2}}{R^{c2}} \right] \right)^2 + \left(a1\left[\frac{E^{b1}}{R^{c1}} \right] \right)^2}{\left(a1\left[\frac{E^{b1}}{R^{c1}} \right] \right)^2} \right)} \right] \tag{3.20}$$

Equation 3.20 is the most general form of the predicted environmental concentration. The coefficients in the above equations are given in Tables 3.16 and 3.17 for water column and pore water concentration, respectively.

The empirical model developed for predicted environmental concentration estimates the concentration of various pollutants in the water column and pore water. The predicted environmental concentration was the adjusted to bioavailable fraction (*BF*) and probability of exposure (*p*) to estimate ecological and human health risk. These are determined in Chapters 4 and 5, respectively.

Chapter 4

ECOLOGICAL RISK ASSESSMENT

4.1. INTRODUCTION

There has been a growing concern to quantify the risk associated with contaminants in air, water, soil and food. These contaminants are also known as *risk agents* or *toxicants* or stressors. They enter the environment through anthropogenic activities including industrialization, improper waste disposal and spills, and contamination of water resources due to leachate from abandoned landfill sites. Until very recently, environmental research was focused on the identification of sources, movement and dispersion of pollution in the environmental media without giving much attention to how these pollutants are transmitted to human and ecological receptors.

An emerging field of research, environmental risk assessment uses an integrated approach to estimate risk quantitatively. The estimate is based on the knowledge of physico-chemical characteristics of the risk agents and their toxicity profiles, routes and exposure pathways, acute (short-term exposure with high dose) and chronic (long-term exposure) receptor response. Such quantitative assessment can be carried out with good understanding of exposure and toxicity assessment of the pollutant release into the media.

The U.S. EPA has developed risk assessment guidelines for carcinogenicity, mutagenicity, developmental toxicity, chemical mixtures, and exposure assessment, which have been published in the Federal Register (U.S. EPA, 1984; 1986a-e). These guidelines provide a framework to promote consistency in conducting various types of risk assessments, but do not discuss the type of modeling tools and specific field measurements that are the basis for quantitative risk assessment.

In this chapter, the concept of ecological risk assessment is introduced with the help of a step by step approach using the case of drilling waste discharges. This chapter deals with different components of risk assessment, but more emphasis is given to risk characterization. The exposure assessment is based on contaminant fate in multimedia and its exposure pathways to receptors. The exposure assessment conponent is an ouput of the contaminant fate modeling methodology which was developed in Chapter 3.

4.2. FRAMEWORK OF ECOLOGICAL RISK ASSESSMENT

The term ecological risk assessment can be defined as "*a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors*" (e.g., U.S. EPA, 1998; CCME, 1997). The U.S. EPA (1998) has provided a comprehensive framework for ecological risk assessment as illustrated in Figure 4.1. This framework is followed to explain the essential elements of ecological risk assessment. As shown in Figure 4.1, there are four basic steps involved in ecological risk assessment. These steps are:

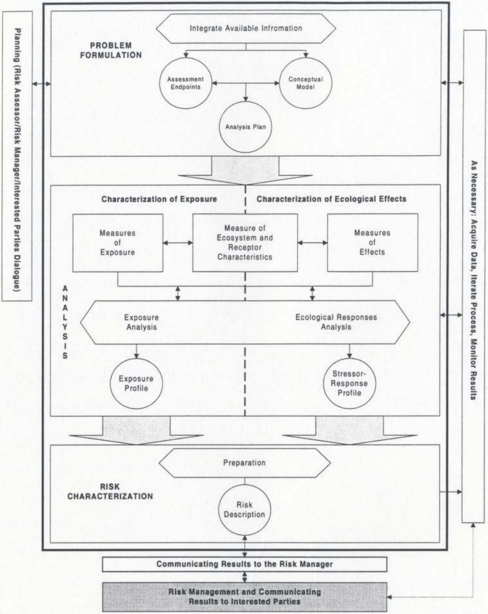


Figure 4.1. The ecological risk assessment framework (U.S. EPA, 1998)

1. Problem formulation
2. Analysis
3. Risk characterization
4. Risk management and communication

Problem formulation is used for data collection and hazard identification. It also deals with the assessment of endpoints (receptors) and the development of a plan for exposure assessment. The second step is the analysis phase, which is the key component of ecological risk assessment. The exposure and toxicity assessments for different ecological entities are the two products of the analysis phase. Once stressor response and exposure profiles are prepared, characterization of risk on short-term and long-term bases can be performed in the next step. Mitigation measures and communicating risk to stakeholders and interested groups are covered in the fourth and the final step of risk assessment. In this chapter the first three steps will be discussed in detail in the perspective of drilling waste discharges in the marine environment.

4.3. PROBLEM FORMULATION

Problem formulation is a process of producing and evaluating hypotheses about the occurrence of ecological effects from anthropogenic activities. It provides a foundation for the ecological risk assessment process. In problem formulation, objectives are defined, the nature of the problem is evaluated, and plans for data analysis and risk characterization are developed. Problem formulation comprises three components: (1) assessment endpoints, (2) conceptual models, and (3) analysis plan.

Drilling waste discharges contain base fluid, heavy metals and some organic priority pollutants. The ecosystems have naturally occurring levels of these pollutants, however, additional amounts of these chemicals can stress the delicate balance necessary for the efficient performance and survival of an ecological community. The background level concentrations in the ecosystem are reported in Table 4.1. The mean water column concentrations are very low in comparison to mean sea level concentrations for all pollutants (see Chapter 3, Table 3.10). The estimated mean arsenic water column concentration is 7.75×10^{-5} µg/L for an impact radius (R) of 50 m and loading rate (E) of 3 g/hr. This is considerably below the mean sea background concentration of 3.7×10^{-2} µg/L. Similar conclusions can be drawn for other pollutants by comparing the predicted water column concentrations with background levels. The other exposure to the ecosystem is through pore water concentration, which is higher than background levels (see Chapter 3, Table 3.12).

Table 4.1. The background concentration level of potential contaminants in drilling waste (Aus-NZ WQG, 1999)

Contaminants	Mean sea background concentrations (µg/L)
Cd	0.044
Ni	0.400
Cu	0.720
Cr	0.079
As	< 0.037
Pb	0.480
Hg	0.054
Naphthalene	0.700

The potential drilling waste contaminants emitted to the marine ecosystem cause environmental damage and have been reported extensively in the literature, e.g., Lee and Nicol (1978), Neff (1979), Rice et al. (1977) and Reish et al. (1976, 1977, 1978, 1979, 1980, 1981, and 1982). Reish et al. (1976-1982) have periodically tabulated toxic effects of heavy metals on individual species. Heavy metals have adverse effects on many species in the marine ecosystem, namely polychaetes, bivalves, gastropods, crabs, algae, crustaceans and fish. For example, chromium (Cr) is toxic to bivalves, crustaceans and fish. The particular effects of heavy metals are inhibition of spawning and suppressed reproduction. The three basic components of problem formulation are explained with the help of examples in the following sections.

4.3.1. SELECTION OF ENDPOINTS

The selection of endpoints should adequately reflect management goals and represent the ecosystem where they live. The management goals are set to save an ecosystem for commercial, economical and recreational reasons. The selection of end points should also be based on ecological relevance and susceptibility to known potential stressors. Ecologically relevant endpoints reflect important characteristics of the system and are functionally related with other endpoints (U.S. EPA, 1992a). These endpoints may be identified at any level of organisation (e.g. individual, population, community, ecosystem and landscape). Ecological entities are not ecologically relevant unless they are currently, or were historically part of the ecosystem under consideration. The relevance is linked to the nature and intensity of potential effects and to the spatial and temporal scales where effects may occur.

Marine organisms are susceptible to heavy metals and other pollutants present in the drilling waste if the concentration is above a certain level. The groups/organisms at the lower trophic levels in the food web are more susceptible. From a management and scientific viewpoint, selection of organisms at various trophic levels could be the right choice for endpoints as they have both economical and ecological importance. Considering the various organisms in Table 4.2 as endpoints may provide better insight to hold the three basic criteria: management goal, susceptibility and ecological relevance. If the whole ecological community is defined as endpoints, it can meet the susceptibility and ecological relevance criteria because the most sensitive species are taken into account. Similarly, considering those ecological entities, which may have commercial value as endpoints (e.g., fish) fulfill the management goal criterion.

The selection of the foodweb as an endpoint is more realistic than defining a single species, or groups, as an endpoint (Husain et al., 2001). The acute and chronic toxicity data for different pollutants are reported in Table 4.2. The LC_{50} or EC_{50} (concentration at 50% adverse effect) are used for measuring short-term or acute toxic effects, which refers to lethal concentration at 50% kill or adverse effect, respectively. The *NOEC* (No observed effect concentration) is used to estimate long-term or chronic effects. The *NOEC* refers to the concentration level at which no adverse effects are expected. Reported data are collected from various sources, which include Reish et al. (1976-82), Hall (2000), U.S. EPA (1976; 1986a-e), Atchison et al. (1977), Holcombe et al. (1976), Booman and Foyn (1996) and Australian and New Zealand water quality guidelines (Aus-NZ WQG, 1999).

Table 4.2. Toxicity data for various contaminants present in the drilling waste

Toxicant	Organisms/Groups	Time (hr)	*LC_{50}* (ppm)	*NOEC* (ppb)	Toxicant	Organisms/Groups	Time (hr)	*LC_{50}* (ppm)	*NOEC* (ppb)
As	*Crustaceans*	96	10		Cd	*Pelecypod* (sp. 1)	96	2.5	
	Bivalves	96	3.5			*Sea star* (sp. 1)	96	> 10	
	Crustacean larvae	96	0.23			*Sea star* (sp. 2)	96	7.1	
	Algae (2 species)	6 - 9 d		1000 - 10000		*Amphipod* (sp. 1)	5 d	0.2 - 0.4	
	Crustacean (3 species)	8 - 51 d	0.89- 70			*Amphipod* (sp. 2)	96	0.32	
	Echinoderms			1500		*Decapod* (sp. 1)	96	6.4 - 6.8	
	Annelids		3 - 7.5			*Decapod* (sp. 2)	7 d	14	
	Molluscs		1.5 - 7.4			*Decapod* (sp. 3)	96	1.3	
	Pelecypod	96	3.49			*Decapod larvae* (sp. 4)	96	0.49	
	Fish		3.4 - 83			*Bivalves*	96	1.6 - 2.5	
Cd	*Polychaetes* (sp. 1)	96	5.8 - 7.5			*Bivalves larvae*	96	1.5	
	Polychaetes (sp. 2)	96	12			*Gastropods*	96	35	
	Polychaetes (sp. 3)	7 d	6.4 - 9.3			*Crustaceans*	96	0.015 - 100	
	Polychaetes (sp. 4)	96	2.5-5.0			*Crustacean larvae*	96	0.25 - 3.8	
	Polychaetes (sp. 5)	96	4.2			*Echinoderms*	96	7.1 - 10	
	Polychaete larvae (sp. 1)	96	0.22			*Fish* (sp. 1)	7 d	16	
	Polychaete juvenile (sp. 2)	28 d	3			*Fish* (sp. 2)	7 d	21	
	Pelecypod (sp. 1)	96	1.48			*Fish embryo* (sp. 3)			< 0.5

Table 4.2. Toxicity data for various contaminants present in the drilling waste (contd.)

Toxicant	Organisms/Groups	Time (hr)	LC_{50} (ppm)	*NOEC* (ppb)
Cd	*Fish* (sp. 4)	96	22	
	Fish larvae	96	0.60 - 14	
	Fish (6 species)	7 - 19 d		108 - 16,000
	Crustacean (19 species)			0.45 - 10400
	Echinoderms (18 species)	7 d		140
	Molluscs (5 species)			30 - 3200
	Annelids (5 species)			7.8 - 1302
	Nematodes			400 - 1000
	Rotifers	72		1040
	Algae (2 species)	10 - 14 d		5.7 - 1780
	Isopods	96	1.25	
	Shrimp	96	0.2 - 0.3	
	Hermit crab	96	0.07	
	Copepod (sp. 1)	96	1.8	
	Copepod (sp. 2)	96	0.01	
	Mysid	96	0.015	
Cr	*Polychaete* (sp. 1)	7 d	1.44 - 1.89	
	Polychaete (sp. 2)	96	0.16-3.2	
	Polychaete juvenile (sp. 2)	96	> 1.0	
	Polychaete (sp. 3)	96	0.3-8.0	
Cr	*Polychaete juvenile* (sp. 3)	96	5	
	Polychaete (sp. 4)	96	4.3	
	Polychaete (sp. 5)	96	2	
	Polychaete (sp. 6)	96	> 5.0	
	Pelecypod	96	57	
	Gastropods	96	105	
	Bivalves	96	57	
	Crustaceans	96	3.4 - 45	
	Echinoderms	7 d	1.7	
	Diatom	72	2.4	
	Macroalgae		360	
	Australian crab		0.3	
	Tidepole fish		2.6	
	Fish (3 species)	14 - 21 d		776 - 14125
	Crustacean (13 species)	7 - 20 d		4 - 3090
	Echinoderms	7 d		2000
	Molluscs (3 species)	7 - 16 d		1600 - 10000
	Sipunculid	11 - 52 d		1995
	Algae (7 species)	7 d		4.8 - 1000
	Brittle star	72	< 3.75	

Table 4.2. Toxicity data for various contaminants present in the drilling waste (contd.)

Toxicant	Organisms/Groups	Time (hr)	*LC*$_{50}$ (ppm)	*NOEC* (ppb)	Toxicant	Organisms/Groups	Time (hr)	*LC*$_{50}$ (ppm)	*NOEC* (ppb)
Cr	*Decapod*	96	30 - 45		Cu	*Bivalves larvae*	48	0.0055	
	Fish (sp. 1)	96	31.2			*Gastropods*	96	0.058	
	Fish (sp. 2)	96	91			*Gastropods larvae*	48	0.11	
	Copepod	96	4.5			*Crustaceans*	96	0.1 - 250	
	Decapod	96	10			*Crustacean larvae*	96	0.048 - 0.17	
	Decapod (larvae)	96	0.17			*Fish larvae*	96	0.028 - 0.13	
	Sea star	96	32			*Fish (6 species)*	11 - 14 d		30 - 260
	Oyster	48	0.611			*Crustaceans (3 species)*	10 - 14 d		1.7 - 42
	Mussels	48	1.20			*Molluscs (7 species)*	5 - 30 d		0.4 - 20000
	Crabs	96	0.247			*Annelids (3 species)*	5 d		17 - 1000
Cu	*Polychaete* (sp. 1)	96	0.2			*Phytoplankton*			0.3 - 10
	Polychaete (sp. 2)	96	0.3			*Hydroid*			0.05 - 14.3
	Polychaete (sp. 3)	96	0.2			*Dinoflagellate*			20
	Polychaete larvae (sp. 1)	96	0.18			*Macroalgae*			10 - 50
	Polychaete larvae (sp. 2)	96	0.3			*Shrimp*			5000
	Amphipod (sp. 1)	96	1.25			*Echinoderms*			10
	Amphipod (sp. 2)	96	1.45			*Oyster (embryos)*	48	0.0053	
	Amphipod (sp. 3)	96	> 10			*Mussels (embryos)*	48	0.0058	
	Decapod	96	250-1000			*Crabs (larvae)*	96	0.049	
	Sea urchin		0.30			*Clams*	96	0.57	

Table 4.2. Toxicity data for various contaminants present in the drilling waste (contd.)

Toxicant	Organisms/Groups	Time (hr)	LC_{50} (ppm)	*NOEC* (ppb)	Toxicant	Organisms/Groups	Time (hr)	LC_{50} (ppm)	*NOEC* (ppb)
Hg	*Fish*	5 - 32 d		7.4 - 160	Hg	*Crustacean larvae*	96	0.0082 - 0.017	
	Crustaceans (3 species)	7 - 35 d	0.0018 - 0.050	0.8 - 10		*Fish* (sp. 1)	96	0.8	
	Echinoderms	7 d	0.02	4		*Fish* (sp. 2)	96		< 860
	Molluscs (7 species)	5 - 12 d	0.004 - 5.07	0.12 - 1014		*Phytoplankton* (sp. 1)	4		1 - 10
	Annelids (2 species)	7 - 28 d	0.017 - 0.09	3.4 - 18		*Phytoplankton* (sp. 2)			2030
	Algae (7 species)			0.9 - 88		*Pelecypod*	37	1.0	
	Polychaete (sp. 1)	96	0.022			*Decapod* (sp. 1)	48	0.01 - 0.0156	
	Polychaete (sp. 2)	96	< 0.1			*Decapod larvae* (sp. 2)	96	0.017	
	Polychaete (sp. 3)	96	0.09			*Pelecypod* (sp. 1)	96	0.4	
	Polychaete (sp. 4)	96	0.07			*Pelecypod* (sp. 2)	96	0.058 - 0.122	
	Polychaete larvae (sp. 1)	96	0.1			*Sea star*	96	0.06	
	Polychaete larvae (sp. 2)	96	0.014		Ni	*Polychaetes*	96	25	
	Copepod	96	0.23			*Bivalve*	96	1.2	
	Decapod	96	0.05			*Bivalve larvae*	48	0.35 - 0.89	
	Bivalves	96	0.058 - 0.4			*Gastropods*	96	72	
	Bivalve larvae	48	0.00065			*Fish*	96	350	30000
	Gastropods	96	32			*Crustaceans* (4 species)	5 - 8 d		640 - 6000
	Crustaceans	96	0.05 - 0.23			*Echinoderms*	7 d		2600

Table 4.2. Toxicity data for various contaminants present in the drilling waste (contd.)

Toxicant	Organisms/Groups	Time (hr)	LC_{50} (ppm)	*NOEC* (ppb)	Toxicant	Organisms/Groups	Time (hr)	LC_{50} (ppm)	*NOEC* (ppb)
Ni	*Molluscs* (5 species)	7 - 12 d		240 - 450000	Pb	*Brine shrimp*		0.085 - 0.25	25 - 180
	Annelid (2 species)	7 d		1540 - 5000		*Fish (larvae)*		0.065 - 0.1	10 - 45
	Pelecypod	96	320			*Mixed marine bacteria*		0.08	20
	Copepod	96	6.0		Zn	*Fish*	7 d		10400
	Decapod	96	47			*Crustaceans* (8 species)	8 - 28 d		250
	Sea star	96	150			*Echinoderms* (8 species)	7 d		460
Pb	*Polychaete* (sp. 1)	96	6.8			*Molluscs* (5 species)	7 - 11 d		15 - 27500
	Polychaete (sp. 2)	96	> 10			*Annelids* (5 species)	7 - 9 d		70 -3260
	Polychaete juvenile (sp. 1)	96	1.2			*Algae* (3 species)	5 - 10 d		13 - 796
	Polychaete juvenile (sp. 2)	96	> 7.5			*Polychaete* (sp. 1)	96	3.5 - 10.7	
	Bivalves	7 d	8.8			*Polychaete* (sp. 2)	96	1.8	
	Bivalves larvae	96	2.5			*Polychaete* (sp. 3)	96	5.5	
	Crustaceans	96	0.58	29 - 51		*Polychaete* (sp. 4)	96	7.1	
	Fish	96	0.52 - 0.8			*Polychaete* (sp. 5)	96	8.1	
	Molluscs	7 d	4.4 - 4.52	880 - 904		*Polychaete* (sp. 6)	96	2.7	
	Annelids (2 species)	28 d	0.84 - 7.55	8		*Polychaete larvae* (sp. 1)	96	1.7	
	Algae (3 species)	10 - 14 d	3.11 - 7.94	8 - 27		*Polychaete larvae (sp. 2)*	96	0.9	
	Bacteria		1.9			*Oyster (embryos)*	48	0.119	

Table 4.2. Toxicity data for various contaminants present in the drilling waste (contd.)

Toxicant	Organisms/Groups	Time (hr)	*LC*$_{50}$ (ppm)	*NOEC* (ppb)	Toxicant	Organisms/Groups	Time (hr)	*LC*$_{50}$ (ppm)	*NOEC* (ppb)
Zn	***Mussels (embryos)***	48	0.175		Zn	***Amphipod***	96	0.58	
	Crabs (larvae)	96	0.456			***Decapod*** **(sp. 1)**	96	9.5 - 13.1	
	Bivalves	96	2.5 - 4.3			***Decapod*** **(sp. 2)**	96	11	
	Bivalve larvae	96	0.31			***Decapod larvae*** **(sp. 2)**	96	1.23	
	Gastropods	96	50			***Decapod*** **(sp. 3)**	96	0.4	
	Crustaceans	96	0.4 - 13			***Sea star***	96	39	
	Crustacean larvae	96	0.18 - 1.2		Ester	***Skeletonema costatum (algae)***		145,600	
	Echinoderms	96	> 10 - 39			***Crustacean*** **(sp. 1)**		87,000	
	Fish **(sp. 1)**	96	9			***Crustacean*** **(sp. 2)**		> 25,000	
	Fish **(sp. 2)**	96	33.5- 40.5			***Crustacean*** **(sp. 3)**		> 32,000	
	Fish **(sp. 3)**	96	60			***Corophium volutator***		> 10,000	
	Copepod	96	1.45		Naphthalene	***Crustaceans*** **(6 species)**	48 - 96	0.85 - 5.7	21
	Fish juvenile **(sp. 1)**	96	11.5 - 14.0			***Molluscs***	96	57	
	Pelecypod **(sp. 1)**	96	2.5 - 4.3			***Annelids***	96	3.8	
	Pelecypod **(sp. 2)**	96	7.7			Karman et al. (1996) have reported *PNEC* value			13.4
	Sea star	96	> 10						

Experimental data can be combined to generate multiple point estimates that can be displayed as stressor-response relationships. If the response of interest is composed of many individual variables, multivariate techniques may be useful. In the case of multiple stressors, the stressor-response relationships are constructed separately and then they are overlapped. A classical stressor-response relationship is shown in Figure 4.2 in which mortality as a response is shown. The intensity of stressors (e.g. dose) is shown by toxicology terms like *NOEC* and LC_{50}. More complex stressor-response relationships can be described using intensity, time, or space. For chemical stressors, the intensity (e.g., concentration) is the most familiar one. Exposure duration may also be used in chemical stressor-response relationships (Sadiq et al., 2001f)

The dosage for 10%, 50% or 90% kill can be easily calculated from the dose response relationships. The lowest observed effect concentration (*LOEC*) and *NOEC* can be derived with higher uncertainty from these relationships. Statistical hypotheses have been used with chronic toxicity tests of chemical stressors that evaluate multiple endpoints. For each endpoint, the objective is to determine the highest test level for which effects are not statistically different from the controls (*NOEC*) and the lowest level at which effects are statistically significant from the control (*LOEC*). The range between *NOEC* and *LOEC* is called the maximum acceptable toxicant concentration (*MATC*). The *MATC* is the geometric mean (GM) of *NOEC* and *LOEC*, which provides a useful reference to compare toxicities of various chemicals. These parameters are also derived based on uncertainty factors (UF) or by using extrapolation models.

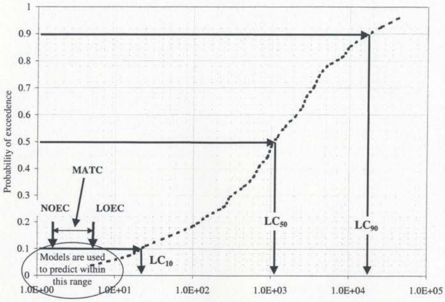


Figure 4.2. Typical stressor-response relationship showing toxicity parameters

4.3.2. CONCEPTUAL MODELS

Conceptual models explain relationships between ecological entities and stressors. They describe exposure pathways, ecological effects and receptors. The complexity of the conceptual model depends on the complexity of the problem: the number of stressors, number of assessment endpoints, nature of effects and characteristics of the ecosystem. Conceptual models provide powerful learning tools and a framework for future applications for risk assessors and also help in modification as knowledge improves.

A set of risk hypotheses predicting relationships among stressors, and exposure and assessment endpoint response is first developed. The stressors in the drilling waste are As, Cd, Cr, Cu, Hg, Ni, Pb, Zn, naphthalene and ester. The assessment endpoint is the food chain of marine organisms depending on the availability of data (Table 4.2). It is assumed that the available assessment endpoint data are representative of the ecological entities in the Atlantic environment. The responses to these stressors are measured in terms of LC_{50} and *NOEC* as given in Table 4.2. The endpoint toxicity data are tabulated at various exposure times. To use this data for further analysis, the following rules and assumptions are made which are illustrated with the help of a flowchart in Figure 4.3.

1. If a range of LC_{50} and EC_{50} data is given, convert data into their geometric mean (GM $= \sqrt{\text{Lowest} \times \text{Highest}}$) using the lowest and highest values (French and French, 1989).

2. If exposure time for LC_{50} (or EC_{50}) is missing, take it as 96 hours.

3. If a range of exposure times is given for LC_{50} (or EC_{50}), use GM of exposure time.

4. Karman and Reerink (1998) have used a time dependence function of LC_{50} for dynamic assessment of the ecological risk of the produced water discharged from oil and gas platforms. In current research the following relationship was used to convert $(LC_{50})_t$ into $(LC_{50})_4$ (Sprague, 1969; Buikema et al., 1982; French and French, 1989).

$$(LC_{50})_4 = (LC_{50})_t \left(\frac{t}{4} \right)^{0.8175} \tag{4.1}$$

where

$(LC_{50})_t = LC_{50}$ at any time t

$(LC_{50})_4 = LC_{50}$ at 96 hour exposure time

5. Divide $(LC_{50})_4$ by an uncertainty factor (UF) of 100 to convert into predicted-no-effect-concentration (*PNEC*) as suggested by Thatcher et al. (1999).

6. If *NOEC* data are given, take it as *PNEC*.

7. If a range of *NOEC* is given, take GM value as *PNEC*.

8. If *NOEC* reported exposure time is other than 96 hours, assume the same value for a 96-hour exposure time.

9. If different values of LC_{50} are given for a group (e.g., fish), assume that the values are for two different species.

10. If *NOEC* and $(LC_{50})_4$ are both available, divide $(LC_{50})_4$ by 100 and take the smaller value as *PNEC*.

The *PNEC* values derived from the above rules are plotted in Figures 4.4 and 4.5 for potential pollutants. The empirical distribution function (EDF) of *PNEC* values is developed for each individual case. These values are assumed to represent any possible exposure pathways, from ingestion of contaminated seawater (bioconcentration) and consumption of the lower trophic level organisms (biomagnification). The *PNEC* values derived from the above rules are for responses, which include survival, inhibition and reduction in growth, inhibition in sexual reproduction, morphological changes, and reduced fertilization and others.

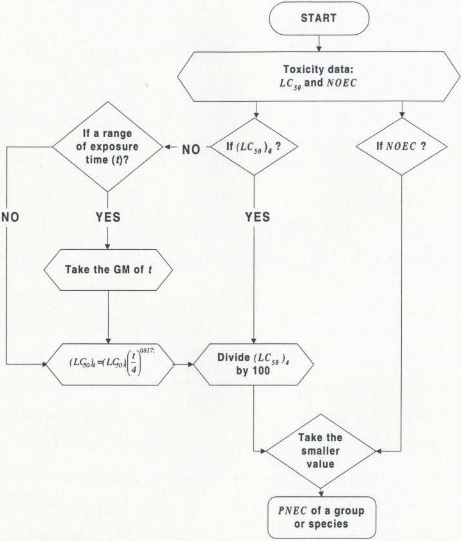


Figure 4.3. Methodology for deriving *PNEC* for a group/species

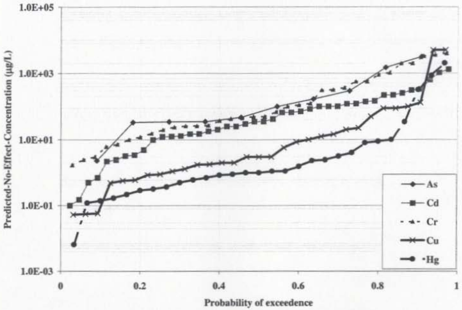


Figure 4.4. Empirical distribution functions of *PNEC* for As, Cd, Cr, Cu and Hg

Figures 4.4 and 4.5 show a wide variation in response of the aquatic community from 10^{-3} to 10^{7} µg/L for different risk agents. From the management goals and risk assessment points of view, the selection of a *PNEC* value which is representative of the whole community is a difficult task. Lenwood et al. (1998) has recommended an arbitrary value of the lowest 10th percentile on empirical distribution function (EDF). The accuracy of these estimates is limited, by data availability. Generally, statistical distributions are used to fit the EDF to account for those cases when data are limited like ester and naphthalene (Husain et al., 2001).

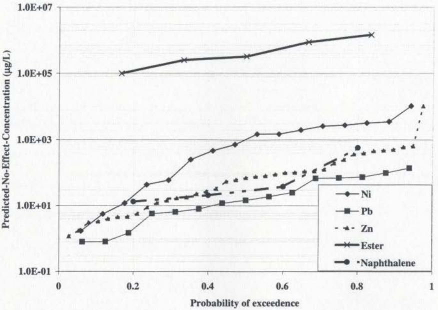


Figure 4.5. Empirical distribution functions of *PNEC* for Ni, Pb, Zn, ester and naphthalene

4.3.3. ANALYSIS PLAN

The analysis plan is the final stage in problem formulation. Risk hypotheses are evaluated to determine how they will be assessed using available data. As risk assessment becomes more unique and complex, the importance of a good analysis plan increases. This includes pathways and relationships identified in problem formulation, and will be pursued during the analysis phase.

4.4. ANALYSIS PHASE

The analysis phase encompasses the two components of risk assessment: characterization of exposures and corresponding effects on endpoints. The analysis phase connects problem formulation with risk characterization. The assessment endpoints and conceptual models developed during problem formulation provide the basic skeleton and structure for the analysis.

Uncertainty evaluation is also an integral part of the risk analysis procedure. The objective is always to describe, and where possible, quantify the errors and limitations associated with exposures and effects. Uncertainty analysis increases both the credibility and the utility of the assessment. Uncertainty characterized during the analysis phase is used during risk characterization and can influence the management decisions. Uncertainty characterization in risk estimation is the main theme of this research.

4.4.1. CHARACTERIZATION OF EXPOSURE

Characterising exposure describes the potential or actual contact of stressors with the endpoints. It is based on the measures of exposure and the ecosystem and also on characteristics of the endpoints. It analyses sources of pollution, distribution of contaminants and mode of contact between stressors and endpoints. At this stage, focus is directed to the identification of pollutant sources, the exposure pathway, the intensity and distribution of stressors spatially and temporally.

Source identification is the first and the most important component of exposure analysis. There are two types of sources. The first is the place from where the stressor originates, e.g., in case of drilling waste discharges the disposal facility outlet is the original source of stressors. The second source is the current location of stressors, e.g., the contaminants transported from the disposal location on the seabed could be the future potential source.

In analyzing the exposure, the background level of the stressor should be measured first to evaluate the effects of a particular source. The location of the source and the environmental media that are first exposed to the stressor need special attention. The source characterization should also consider whether other constituents emitted by a source influence transport, transformation, or bioavailability of the stressor of interest. The primary source of stressors associated with drilling waste is the disposal outlet in the marine ecosystem. The steady state fate models consider not only the primary source, but in addition the continuous contributions from already deposited waste on the seabed, to determine pore water and water column concentration.

In the case of drilling waste, the heavy metals speciate into various oxidation states. These metal species can behave very differently in the marine environment. The toxicity profile of Cr (III) is different from Cr (VI). Similarly As and other heavy metals are also present in various forms in the marine system. The physico-chemical parameters like hardness, pH, temperature and presence of other compounds in the marine environment affect the speciation of metals (Aus-NZ WQG, 1999). In this study metal speciation is not taken into account.

Bioavailability is the extent to which a substance can be absorbed by living organisms and can cause an adverse physiological or toxicological response. For ecological risk assessment involving sediments, the definition includes the extent that the substance can desorb, dissolve or dissociate. The uptake of metals from sediments and water is a dynamic process that involves all levels of the food web (Bernhard, 2000). Organisms take bioavailable metal from sediments and water through external surfaces, ingestion of contaminated sediments and inhalation of vapor phase metals. In addition, organisms take bioavailable metals from their food. A fish can take up metal directly from environmental media through its gills, its skin or through sediment ingestion (Campbell et al., 1988).

In this research, the metal concentrations in sediment pore water are calculated using an aquivalence based approach. The pollutant bioavailable concentration is determined by dissolved and/or bioavailable fraction of the metals. The U.S. EPA (2000a) used leaching factors (*LF*) to determine the bioavailable fraction of heavy metals in the pore water for drilling waste discharges. The U.S. EPA (1996b) defined another term called conversion factor (*CF*) to determine the dissolved fraction in metals. Table 4.3 provides a summary for leaching factors and conversion factors for heavy metals. The predicted environmental concentration (*PEC*) in pore water is adjusted for bioavailable fraction by multiplying by a factor. For organic compounds (base fluid and naphthalene) the estimated concentration is assumed to be completely dissolved and biologically available.

The second objective of exposure analysis is to describe the spatial and temporal distribution of stressors in the environment. Stressor distribution in the environment is examined by evaluating pathways from the source as well as the formation and subsequent distribution of secondary stressors. The evaluation of chemical stressor distribution in the environment is related to partitioning in different media. Ecosystem characteristics influence the fate of all types of stressors. The stressor distribution in the environment is calculated by monitoring or by using fate models or a combination of the two. In this research, a probabilistic fugacity/aquivalence based model was used to predict the concentration in the pore water and water column.

Table 4.3. Factors used to determine the bioavailable fraction in saltwater

Heavy Metals	*LF* (U.S. EPA, 2000a)	*CF* (U.S. EPA, 1996b)
As	0.005	1.000
Cd	0.110	0.994
Cr	0.034	0.993
Cu	0.0063	0.830
Hg	0.018	0.85
Ni	0.043	0.990
Pb	0.020	0.951
Zn	0.0041	0.946

The selection of the foodweb as an endpoint depicts a realistic picture of the aquatic environment where survival of organisms at higher trophic levels depends on the existence of sensitive organisms. The exposure of some of the sensitive organisms in the foodweb might lead to high risk of reduction of commercial aquatic life. The organisms do not necessarily stay close to the impact site and move within the whole area under study. Stansbury (1991) considered the migration rate of finfish and shellfish to determine the exposure probability (*p*) for characterization of ecological risk for dredged material disposal in the ocean. The U.S. EPA (2000a) calculated exposure probability by dividing the volume of the plume by the total volume in which fish are expected. A similar approach was used in this research to estimate the probability (*p*) of exposure, which is defined as the ratio of impact area to the total area of the region under consideration. Therefore the exposure concentration becomes:

$$EC = PEC \times p \times BF \tag{4.2}$$

where,

EC = Exposure concentration;

p = Probability of exposure;

BF = Bioavailable fraction; and

PEC = Predicted environmental concentration (calculated from equation 3.20)

Pore water concentrations are higher than water column concentration by orders of magnitude due to the hydrophobic nature of drilling waste. Therefore, the major ecological concerns related to drilling waste are benthic organisms, which are at a lower trophic level in the food web. Figure 4.6 describes a conceptual illustration of marine aquatic life living close to a drilling waste plume.

The third objective is to describe the contact between stressor and receptor. For chemicals, contact is quantified as the amount of the chemical ingested, inhaled, or material applied to the skin. Some stressors must not only be contacted but also must be internally absorbed. In that case uptake is evaluated by considering the amount of stressor internally adsorbed by an organism. The organisms have different capacities to absorb depending on the physico-chemical characteristics of the pollutants and the uptake processes within the body. In this research the exposure concentrations are assumed to be taken up by endpoints with 100% absorption efficiency for simplicity.

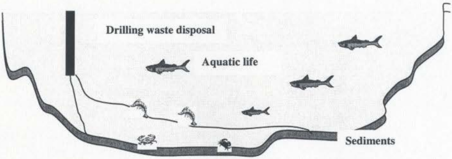


Figure 4.6. A conceptual model of marine foodweb and drilling waste plume

4.4.2. CHARACTERIZATION OF ECOLOGICAL EFFECTS

This step evaluates the relationship between stressor levels and ecological effects or response. Information on the probability that effects may occur as a result of exposure to that stressor, and on their linkages, is collected. The stressor-response relationships used in a particular assessment depend on the scope and nature of the ecological risk assessment as defined in the problem formulation stage. The shape of the stressor-response curve is useful to determine the presence of effects for evaluating risk.

Stressor-response data collected from laboratory experiments are preferably fitted to the statistical models from which risk can be estimated for a selected dose. In practice, due to lack of data, the models like one-hit, multi-stage, multi-hit and Weibull are found to be useful in estimating risk. The details of the models can be found in Suter (1993, 1996) and Covello and Merkhofer (1993). Many empirical and process based approaches are also available for linking measures of effect to assessment endpoints. These approaches are used when an adequate database is available.

For characterisation of ecological effects, the CHARM model uses toxicity test results of algae, crustaceans and/or fish (Thatcher et al., 1999). Only chronic *NOEC* and acute EC_{50} or LC_{50} are used, but *NOEC* results are preferred, if available. The CHARM model does not accept other chronic test results like *LOEC*, EC_{10} or LC_{10}. The CHARM model also requires an exposure time of at least 96 hours.

In this research, characterisation of ecological response was based on *PNEC* data as shown in Figures 4.4 and 4.5. The EDFs were fitted to the statistical distributions using BEST-FIT (1993). The goodness of fit (GoF) of the model was determined by the Anderson-Darling GoF test, which described the best-fit distribution. The criterion for the fit of a distribution in the Anderson-Darling test used was A-statistics. The 5% and 10% critical A* values were 0.752 and 1.035, respectively. If the calculated A* was less than critical values, the data were distributed to that particular distribution for which the test was performed. The lognormal distribution was found to be the best distribution overall for response data (*PNEC*) among 21 different candidate distributions. Other distributions, which also fit to the data, were Pearson Type VI and Gamma distributions. Figure 4.7 shows a lognormal fit to the *PNEC* data for Zn.

Table 4.4 summarises the statistics for *PNEC* data for various pollutants. The mean (μ_x) and standard deviation (σ_x) for lognormal fit are also provided. The A-statistics for response of all different contaminants except Hg is within the 5% critical value, but the lognormal fit has the lowest A-statistics value among the candidate distributions. Data for naphthalene and ester are limited, so any conclusion about the distribution choice is difficult. To make our case more generalised *PNEC* response distributions are assumed lognormally distributed for all contaminants.

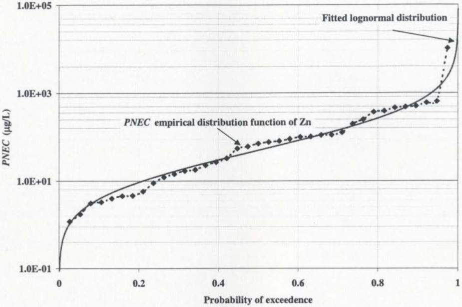


Figure 4.7. Lognormal distribution fit to the *PNEC* empirical distribution (Zn)

An ecological objective can be defined in terms of events, where an event consists of three components: object, endpoint and level (Jooste, 2000). For example, more than 10% decrease in biodiversity may cause an irreversible change in the ecosystem. Therefore, an ecological objective in the event form can be defined as {foodweb biodiversity, reduction or damage, 10%).

Table 4.4. Statistics for lognormally distributed response

Toxicant	Data Points (N)	Lognormal rank among candidate distributions	A^*	Mean (μg/L) (μ_s)	Std. dev. (μg/L) (σ_s)
As	10	1	0.3368	703.3	4.873
Cd	42	2	0.3497	274.5	2.904
Cr	34	1	0.4420	897	9.458
Cu	31	1	0.5216	235	10.210
Hg	29	1	1.0950	59.6	1.944
Ni	16	3	0.7519	8.866	215.812
Pb	15	3	0.3968	53.2	198
Zn	37	1	0.3550	358.1	2.543
Naphthalene	4	2	0.4775	143.5	388.8
Ester	5	3	0.2294	623.861	749.329

$A^*_{critical\ 5\%} = 0.752$ and $A^*_{critical\ 1\%} = 1.035$ μ_s = mean of *PNEC* values σ_s = std. dev. of *PNEC* values

A criterion for safety level was set at the lowest 10th percentile on response distributions to save 90% of the ecological community or to maintain biodiversity in the aquatic foodweb. 10th percentile response should be more than exposure concentration. To determine the 10th percentile level and its associated uncertainty, bootstrapping was performed on the *PNEC* derived data, as shown in Figures 4.5 and 4.6 (Sadiq et al., 2001d).

Bootstrapping relies on an analogy between the sample and the population from which the sample is drawn. Bootstrapping involves re-sampling the data with replacement many times in order to estimate the statistics of interest (Sadiq et al., 2001e). 1000 bootstrap samples (*B*) were performed for each contaminant *PNEC* data. For each bootstrap run, mean (μ_Y) and standard deviation (σ_Y) were calculated assuming a lognormal distribution. The 10th percentile on lognormal distribution fit calculated for each bootstrap run with the help of a set of mean and standard deviation. The mean (μ_{10}) and standard deviation (σ_{10}) of 10th percentiles were calculated from 1000 (B) bootstrap runs. The statistics of criteria *PNEC* value is derived to save the whole foodweb (Table 4.5). The macro was written in Minitab (1998) and given in Appendix-A1. The formulation of estimating means and standard deviation of *PNEC* criteria value is given in equation 4.3.

$$\left.\begin{aligned}
Y_i &= \log\,[X_i] \\
\mu_Y &= \mathrm{mean}\,[Y_i] \\
\sigma_Y &= \mathrm{standard\ deviation}\,[Y_i] \\
X_{10} &= e^{(\mu_Y - 1.2815 \times \sigma_Y)} \\
\mu_{10} &= \sum (X_{10})/B \\
\sigma_{10} &= \sum (X_{10} - \mu_{10})^2/(B - 1)
\end{aligned}\right\} \qquad (4.3)$$

where

X_i = *PNEC* values derived from Table 4.2 and shown in Figures 4.5 and 4.6.

Y_i = Log transformed *PNEC* values

μ_Y = Mean value of data by fitting lognormal distribution for each bootstrap run (B)

σ_Y = Standard deviation of data by fitting lognormal distribution for each bootstrap run

X_{10} = 10th percentile value on lognormal distribution for each bootstrap run

B = No. of bootstrap runs (1000)

N = No. of *PNEC* values for each data set ($i = 4 - 42$; see Table 4.4)

μ_{10} = Mean of *PNEC* criteria value

σ_{10} = Standard deviation of *PNEC* criteria value

The *PNEC* criteria values were calculated and compared with the most stringent U.S. Federal water quality criteria (U.S. EPA, 2000a), CCME (1999) and Aus-NZ WQG (1999) used for marine water.

Table 4.5. Comparison of *PNEC* response criteria value parameters and other international standards (µg/L)

Toxicant	μ_{10}	σ_{10}	U.S. (2000a) FWQC	CCME (1999)	Aus-NZ (1999) WQG
As	12.12	11.10	14.00	12.50	2.40
Cd	1.87	1.10	9.30	0.12	1.70
Pb	2.12	1.65	8.10	7.00	0.80
Cr	5.77	2.62	50.00	1.50	3.10
Cu	0.20	0.12	2.40	4.00	0.32
Hg	0.075	0.041	0.025	0.10	0.029
Ni	25.82	38.80	8.20	25.00	32.60
Zn	4.24	1.80	81.00	30.00	2.70
Naphthalene	13.04	36.08		1.40	8.40
Ester	177.475	877.810			

4.5. RISK CHARACTERIZATION

Risk characterization is the most important step in ecological risk assessment and involves planning and analysis of predicted adverse effects of assessment endpoints. Risk characterization develops the relationships between stressor and effects. The risk assessor uses the results of the analysis phase to develop an estimate of the risk posed to the ecological entities selected as assessment endpoints. After assessing the risk, the assessor describes the risk estimate in the context of the significance of adverse effects. The risk assessor also identifies the uncertainties and assumptions in the risk assessment. The risk characterization provides information for environmental decision making. Risk characterization includes risk estimation and risk description as discussed in the following sections.

4.5.1. RISK ESTIMATION

Risk estimation is the process of integrating exposure and response data and evaluating any associated uncertainties. This process uses exposure and stressor response profiles according to an analysis plan. A general methodology for risk estimation is shown in Figure 4.8. Risk estimation can be done using one or more of the following techniques:

1. Field observational studies;
2. Categorical rankings;
3. Comparisons of single-point exposure and effects estimates;
4. Comparisons incorporating the entire stressor-response relationship;
5. Incorporation of variability in exposure and/or effects estimates, and
6. Process models that rely partially or entirely on theoretical approximations of exposure and effects

Field Observational Studies

This technique provides empirical evidence which links exposure to response. Field surveys measure changes in the natural setting by collecting exposure and effects data for different ecological entities in the problem formulation phase. The main advantage of field surveys is that multiple stressors and very complex ecosystem relationships can be measured which are difficult to perform in laboratory studies (U.S. EPA, 1998; U.S. DOE, 1998). This technique should be used for validating modeling results. The field observational and monitoring studies are popular in offshore drilling waste disposal due to difficulties in modeling the complexities of transport and fate behavior of the drilling waste.

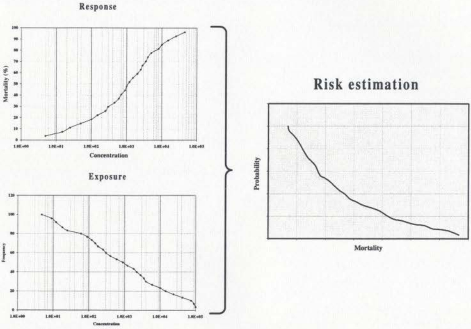


Figure 4.8. A general approach for risk estimation using exposure-response relationship

Categories and Rankings

Qualitative evaluation techniques are performed through professional judgment, which are very popular in risk estimation. Risk can be categorized as low, medium, high or ranked on some numeric scale. This approach is adopted in case of limited data availability or when data can not be expressed in quantitative form. Ranking techniques translate qualitative judgment into mathematical forms. Fuzzy set theory is generally used to rank the risk from different stressors by considering the degree of immediate risk, duration of impacts, and prevention and remediation management. Lu and Hu (1999) have used the fuzzy approach to analyze eutrophication effects for water quality assessment in Taiwan.

Single-Point Exposures and Effects Comparisons

When sufficient data are available to estimate exposure and response, the most common technique is to take the ratio. Typically the ratio or quotient is expressed by $\frac{\text{exposure concentration}}{\text{effects concentration}}$. The advantage of the quotient method is that it is simple and easy to understand. The quotient method is also used to integrate risks of multiple chemical stressors. It can be obtained by dividing each exposure level with corresponding toxicity endpoints (LC_{50}, EC_{50}, *NOEC*, *LOEC*, *MATC* etc.) and generating quotients for the individual constituents in a mixture. The toxicity of a chemical mixture may be greater or less than predicted from the toxicities of individual constituents of the mixture. The quotient addition approach assumes that toxicities are additive or approximately additive. This assumption may be the most applicable when the modes of action of chemicals in a mixture are similar. There is evidence that even with chemicals having dissimilar action, additive or near-additive interactions are common (U.S. DOE. 1998; Jooste, 2000; McCarty and Mackay, 1993; Konemann, 1981; Broderius, 1991 etc.).

However the U.S. EPA (1998) has cautioned that assuming chemicals in a mixture act independently might cause erroneous conclusions. When the modes of action for constituent chemicals are unknown, the assumption and rationale should be clearly stated. In most cases, the quotient method does not explicitly consider uncertainty. Some uncertainties can be incorporated into single-point estimates to provide a statement of likelihood that the effects point estimate exceeds the exposure point estimate. A comparison of deterministic values of exposure concentrations and *PNEC* are shown in Figure 4.9a. The uncertainty in exposure and response estimates can also be incorporated (see Figures 4.9 b and c). If uncertainty is considered in exposure and response, the CDF of *HQ* can be established and the probability of exceeding 1, i.e., $p(HQ \geq 1)$ can also be calculated.

Mukhtasor et al. (2001) used a risk characterization approach by generating the CDF of response (LC_{50}) of fish and crustaceans. They compared the CDF of response with the CDF of exposure to determine the uncertainty in risk estimates. Some attempts have also been made to take into account the uncertainty of the pollutant concentration in seawater (Karman and Reerink, 1998). In the CHARM model, the uncertainty is addressed very vaguely. The calculated hazard or risk quotient (*HQ/RQ*) is divided and multiplied by 3 to define the lower and upper 95% confidence levels, respectively (Thatcher et al., 1999).

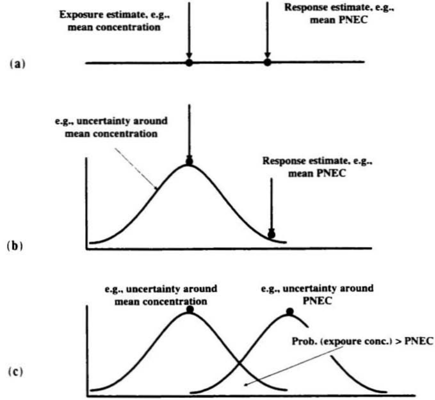


Figure 4.9. Risk estimation techniques (U.S. EPA, 1998)

(a) Comparison of point estimates;
(b) Comparison of point estimate of a stressor-response relationship with uncertainty associated with an exposure point estimate; and
(c) Comparison of point estimates with associated uncertainties

Comparisons Incorporating the Entire Stressor-Response Relationship

If a dose response curve is available, then risk can be determined at different levels of exposure as shown in Figure 4.10. The advantage of this technique is that it considers the whole range of stressor-response relationship for one species. In this method calculating uncertainty bounds on the stressor-response or exposure estimates can incorporate uncertainty which is lacking in the quotient method.

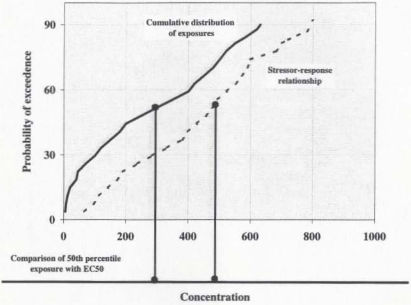


Figure 4.10. Risk estimation considering variability in stressor-response relationship

Comparisons Incorporating Variability in Exposure and/or Effects

If the exposure or stressor-response profiles are used to express the variability in exposure or effects, then many different risk estimates can be calculated. Variability in exposure can be used to estimate risks to moderately or highly exposed members of a population being investigated, while variability in effects can be used to estimate risks to average or sensitive population members. A major advantage of this approach is its ability to predict changes in the magnitude and likelihood of effects for different exposure scenarios and thus provide a means for comparing different risk management options. Comparing distributions also allows one to identify and quantify risks to different segments of the population (Figure 4.11). Husain et al. (2001) used a similar approach for estimating the risk of soot deposition in the Persian Gulf. Lenwood et al. (1998) and Solomon et al. (1996) used LC_{50} values to plot the CDF of response and compare with the CDF of exposure.

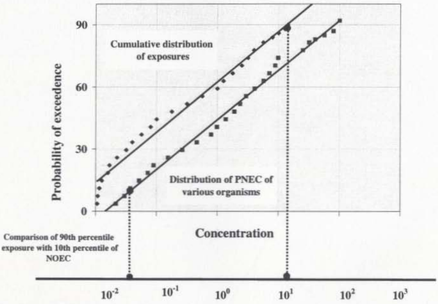


Figure 4.11. Risk estimation technique considering variability in exposure and response

Application of Process Models

Process models integrate both exposure and effects information to estimate risk. During risk estimation, it is important that both the strengths and limitations of a process model approach be highlighted. Brody et al. (1989 and 1993) linked two process models to integrate exposure and effects information and forecast spatial and temporal changes in forest communities and their wildlife habitat value.

4.5.2. PROPOSED METHODOLOGY FOR RISK ESTIMATION

In the current research, risk was estimated by calculating a hazard/risk quotient. The hazard or risk quotient can be calculated by taking the ratio of exposure concentration (*EC*, equation 4.2, adjusted predicted environmental concentration from output of fugacity/aquivalence based models) and the 10th percentile on response CDF (*PNEC* criteria value, equation 4.3). The uncertainty in 10th percentile response level was estimated from Table 4.5.

$$HQ = \frac{Exposure\ \ concentration(\,adjusted\ \ 95^{th}\ \ percentile,\ from\ regression\ \ model\,)}{10^{th}\ \ percetile\ \ on\ PNEC\ log\ normal\ CDF} \qquad (4.4)$$

The hazard quotient/risk quotient was calculated from the above equation. A coefficient value more than 1 shows the probability or risk of adverse effects. An empirical distribution function of *HQ* can be developed from equation 4.4, which shows uncertainty in hazard quotient estimates. The *HQ* critical value of 1 means that 90% of the ecological community is protected 95% of the time.

The quotient method is useful in explaining the relative risk but cannot estimate and quantify risk, which is important in management decisions. The CHARM model is used extensively in the North Sea as a tool for determining ecological risk of offshore discharges. The CHARM model determines *HQ/RQ* for a given compound and relates the estimate to a risk value by the following relationship:

$$Risk = \int_{y=0}^{ln(RQ)} \left\{ \frac{1}{S_m \sqrt{2\pi}} \; e^{\frac{(y-X_m)^2}{2S_m^2}} \right\} \tag{4.5}$$

where

X_m = Average of the lognormally transformed data = 2.85

S_m = Standard deviation of the lognormally transformed data = 1.74

y = Variable to describe the normal probability curve

Karman et al. (1996) and Karman and Reerink (1998) used a similar relationship to convert the *HQ/RQ* into risk values for produced water discharges. The above relationship is calibrated to a given *RQ* value of 1 at an acceptable risk level of 5% (Thatcher et al., 1999). Karman et al. (1996) used 17 chemicals to calibrate this relationship. The organic chemicals include oil, benzene, phenol, toluene, xylene, ethylbenzene, methanol, naphthalene, cresol, and PCP; and heavy metals include Cr, Hg, Ni, Pb, Cd, Cu and Zn.

This calibration level is a political choice, which can be used as an acceptable risk. The mean (X_m = 2.85) and standard deviation (S_m = 1.74) values are adjusted to calibrate to a 5% acceptable risk. In this research the empirical distribution function of *HQ* calculated from equation 4.4 will be converted into risk estimates using equation 4.5. Figure 4.12 shows a proposed methodology for converting *HQ* into corresponding risk values for a single contaminant.

The CHARM model uses a chemical specific approach in which all chemicals are dealt with separately. The effect of each waste component is integrated by considering each chemical effect as independent of the others. The assumption of independent mode of action enables the use of statistical calculation rules for combining independent probabilities (Jooste, 2000). For example, for the mixture of three chemicals, total risk can be calculated by the following equations:

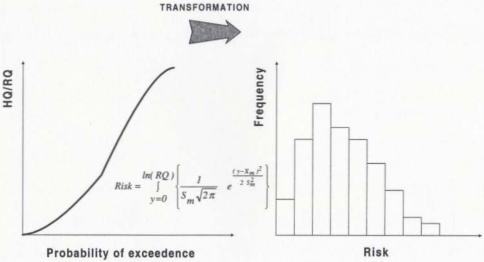


Figure 4.12. Transformation of *HQ/RQ* into risk using a lognormal function

$$Risk\,(A+B) = Risk\,(A) + Risk\,(B) - Risk\,(A) \times Risk\,(B) \quad \text{and} \tag{4.6}$$

$$Risk\,(A+B+C) = Risk\,(A+B) + Risk\,(C) - Risk\,(A+B) \times Risk\,(C) \tag{4.7}$$

Similarly, the relationships for four and more pollutants can be developed.

For a waste which contains more than 4 to 5 chemicals, the synergistic and antagonistic effects are significantly negligible (Jooste, 2000). The total hazard is not the addition of individual *HQ/RQ* (Karman and Reerink, 1998). The *HQ/RQ* are first converted into their corresponding risk values and then total risk is estimated by considering the components to be statistically independent events (e.g., equations 4.6 and 4.7). The drilling waste is an amalgamation of toxic compounds. The *HQ/RQ* will be calculated for individual contaminants and then converted into the risk values (equations 4.4 and 4.5). The risk values are then grouped together to estimate the total risk posed to the ecosystem from drilling waste discharges.

4.5.3. RISK DESCRIPTION

The risk estimation results are interpreted in this phase. The risk assessor needs to comprehend the available information about risk estimates of endpoints. Risk description includes an evaluation of lines of evidences to support or refute the risk estimates and interpret the significance of adverse effects. The description of risk is an important step and the results of risk estimation are used in Chapter 6 for risk management in risk-cost tradeoff analysis.

Chapter 5

HUMAN HEALTH RISK ASSESSMENT

Offshore drilling operations may pose two types of human health risks: exposure of toxic chemicals to workers on offshore drilling rigs through inhalation, ingestion and skin contact; and exposure related to consumption of contaminated seafood due to discharge of drilling waste chemicals in the ocean environment. This chapter focuses on human health risk assessment, based on exposure to carcinogenic and non-carcinogenic contaminants through consumption of contaminated seafood. A description of adverse human health effects due to consumption of contaminated fish is provided in this chapter.

5.1. INTRODUCTION

The framework of human health risk assessment includes hazard identification, exposure and toxicity assessment, risk characterization and risk communication. A probabilistic approach is employed for risk characterization and estimation of uncertainty while developing a methodology for human health risk assessment.

An organization chart of this chapter is illustrated in Figure 5.1. A description of contaminants found in drilling waste and their toxicity profile are presented from an adverse human health effects point of view. Human health risk assessment can be estimated based on cancer and non-cancer models. The input parameters required in these models are discussed in detail. The risk characterization involves uncertainty in the estimates of risk due to input parameter uncertainties. The U.S. EPA (1999b) human health risk assessment (HHRA) approach for drilling waste discharges is also presented. A brief description of probabilistic and fuzzy based approaches is given in the context of HHRA. In the end, the proposed methodology for HHRA is presented.

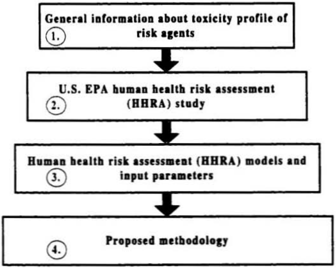


Figure 5.1. Chapter organization for human health risk assessment

5.2. TOXICITY PROFILE OF RISK AGENTS

Human health risk assessment can be performed for those contaminants for which oral reference dose *RfD* (for non-carcinogenic effects) and slope factor *SF* (for carcinogenic effects) have been established. Drilling waste contains heavy metals, priority pollutants and base fluid, as discussed in previous chapters. The oral reference dose and slope factor for any synthetic base fluid has not been established for exposure through ingestion. Therefore, traditional human health risk assessment methodology can not be applied to esters (U.S. EPA, 1999b).

The toxicity of various contaminants is established through laboratory studies on animals or sometimes on human tissues. The epidemiological data are another important source for estimating toxicity effects on humans. To establish and collect the evidence of toxicity effects on humans for a particular contaminant is very difficult because humans are exposed to various contaminants simultaneously. Laboratory studies are used when animals are exposed to one specific contaminant at higher dosage and then effects are extrapolated through mathematical techniques for humans. Different modes of action in various animals lead to questions of the variability of intra and inter species extrapolations. Epidemiological studies are considered the most authentic source to estimate adverse human health effects because extrapolations and uncertainty factors are not involved in the analysis. The collection of epidemiological data is very expensive and scarce. The U.S. EPA (2001) has developed a database, *Integrated Risk Information System* (IRIS), for various contaminants and has reported their human health effects through ingestion, inhalation and dermal contact, which are collected through peer-reviewed sources. The contaminants are categorized based on the toxicity information available through animal or human studies as given in Table 5.1.

Table 5.1. Categorization of contaminants for human health risk assessment

Human evidence	Animal evidence				
	Sufficient	Limited	Inadequate	No data	Evidence of no effect
Sufficient	A	A	A	A	A
Limited	B1	B1	B1	B1	B1
Inadequate	B2	C	D	D	D
No data	B2	C	D	D	E
Evidence of no effect	B2	C	D	D	E

The contaminants under "A" category are those for which there is sufficient evidence of adverse health effects including human cancer and non-cancer ailments. The information collected from human epidemiological studies has more weight. If a contaminant has sufficient evidence of adverse health effects through epidemiological studies and even if there is no evidence from animal studies, the contaminant will still be categorized as "A". The group "B" (B1 and B2) is for limited and inadequate evidences (through human and animal studies) of adverse effects. The categories "C" and "D" are for those contaminants that lack sufficient evidence from human and/or animal studies. If there are no data and no evidence through animal and human studies the contaminant is categorized as "E".

Based on the information from *IRIS* the data for reference doses (*RfD*) and slope factor (*SF*) were collected for heavy metals and naphthalene (U.S. EPA, 2001). The arsenic (As) is the only risk agent that has sufficient evidence of cancerous effects in the list of drilling waste contaminants. It is categorized as "A" type of contaminant. The slope factor of arsenic is 1.5 (mg/kg-day)$^{-1}$. The human health cancer risk was studied for arsenic only. Similarly, the oral reference doses for copper (Cu) and lead (Pb) are not established yet. The non-cancer effects were studied only for those contaminants for which *RfD* is available. The non-cancer risk will be estimated for As, Cd, Cr, Hg, Ni, Zn and naphthalene. Table 5.2 summarizes the reference doses and slope factor of contaminants of concern.

5.3. HUMAN HEALTH RISK ASSESSMENT

The HHRA starts with hazard identification and ends at risk communication. LaGrega et al. (1994) have classified quantitative human health risk assessment into the following five components:

1. Hazard identification;
2. Exposure assessment;
3. Toxicity assessment;
4. Risk characterization; and
5. Risk communication

5.3.1. HAZARD IDENTIFICATION

Human health risk assessment generally deals simultaneously with a number of risk agents, which are emitted from a contaminated source. The hazard identification examines the data of all contaminants detected from the source and emphasizes the chemicals that are of concern. Risk assessment requires knowledge of the source of contamination, concentration of contaminants and transport mechanisms, i.e., how they will reach the receptor.

Naphthalene and heavy metals including As, Cd, Cr, Hg, Ni and Zn are identified as the risk agents that may cause adverse human health effects through an oral route.

5.3.2. EXPOSURE ASSESSMENT

The exposure assessment is the second stage in quantitative human health risk assessment. It estimates the contaminant exposure to the population at risk. To understand the source of contamination, exposure assessment begins with delineation of the sources (e.g., contaminated sediment pore water and/or water column near the drilling waste disposal site) and their spatial distribution (impact area, A_*). When the chemicals are released it is necessary to understand how they migrate to a potential receptor. The exposure assessment encompasses various steps, which include identifying exposure pathway, process mechanisms, exposed populations and scenarios of exposure point and receptor dosage.

Environmental Pathway

To identify exposure pathways, the following elements are studied:

1. Source (e.g., disposal site);
2. Chemical release mechanism (e.g., offshore disposal of drilling waste);
3. Transport mechanism (e.g., advection, deposition, resuspension at the disposal site);
4. Transfer mechanism (e.g., adsorption to sediments, leaching into pore water);
5. Transformation mechanism (e.g., biodegradation);
6. Exposure point (e.g., contaminated fish);
7. Receptor (e.g., general public); and

Table 5.2. Toxicity profile of drilling waste contaminants from human health risk point of view

Risk agents	Carcinogenic classification	*RfD* (mg/kg-day)	Critical effects	*SF* (mg/kg-day)$^{-1}$
As	A Human carcinogen	3E-4	Hyperpigmentation, keratosis and possible vascular complications	1.5 Sufficient evidence from human data. An increased mortality from multiple internal organ cancers (liver, kidney, lung, and bladder) and an increased incidence of skin cancer were observed
Cd	B1 Probable human carcinogen	5E-4	Significant proteinuria for human studies involving chronic exposures	
Cr	D Carcinogenicity by the oral route of exposure cannot be determined	3E-3	Not reported	
Cu	D There are no human data and inadequate animal assays data for copper compounds			
Pb	B2 Possible human carcinogen		Changes in blood level of certain enzymes, alters neurobehavioral development of children	
Hg	C No evidence in humans but cases in animals	3E-4	Developmental neurologic abnormalities in infants	

Table 5.2. Toxicity profile of drilling waste contaminants from human health risk point of view (Contd.)

Risk agents	Carcinogenic classification	*RfD* (mg/kg-day)	Critical effects	*SF* $(mg/kg\text{-}day)^{-1}$
Ni		2E-2	Decreased body and organ weights	
Zn	D Not classifiable as to human carcinogen due to lack of evidence in human and animals	3E-1	Decrease in erythrocyte superoxide concentration in adult females after 10 weeks of Zn exposure	
Naphthalene	C Possible human carcinogen. Inadequate data of carcinogenicity in humans, and the limited evidence of carcinogenicity in animals	2E-2	Decreased mean terminal body weight in males	

8. Exposure route (e.g., ingestion of contaminated fish)

The above steps are integrated to determine the environmental exposure pathway of drilling waste contaminants to reach the general public. A conceptual model for human exposure through contaminated fish is given in Figure 5.2.

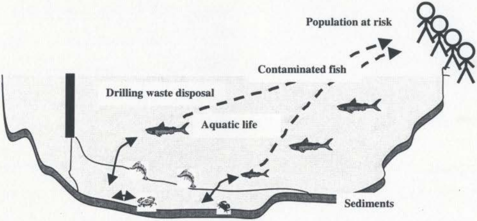


Figure 5.2. Exposure pathway through ingestion of contaminated fish - a conceptual model

Process Mechanisms

The release of drilling waste from a drilling rig is through a disposal outlet. Different processes are involved in transport, transfer and transformation of contaminants in the marine environment. The transport mechanisms may include advection, deposition, and resuspension of drilling waste. The transfer mechanisms include adsorption of chemicals to sediments and biota, and leaching of chemicals back into the water column and pore water.

Potentially Exposed Population

The potentially exposed population could be a community living close to the affected site (fishermen), future population, special population (e.g., infants) or general public. In this study the general public was assumed to be the potentially exposed population.

Exposure Scenarios

When the exposed population and exposure pathways are identified through a conceptual model, the exposure estimates are made through various discharge scenarios. These discharge scenarios may include 10%, 8.5%, 7%, 5.5% and 4% attached base fluid discharge conditions of drilling waste.

Exposure Point Concentrations

The concentrations of contaminants are estimated at the exposure point or location (through exposure pathway). The monitoring values, e.g., bioassays of fish found at the contaminated site may be the best estimates. In this study, the modeling results will determine the exposure point concentrations. The predicted environmental concentration (PEC) adjusted for bioavailable fraction (BF) and exposure probability (p) can be used as the exposure point concentration in the water column and pore water, which is assumed uniformly distributed over the whole area under study.

Receptor Doses

The final step in the exposure assessment is to estimate the dose of chemicals to which the receptors are actually exposed. The Guidelines for Exposure Assessment (U.S. EPA, 1992b) has defined the oral route for ingestion of contaminated food in Figure 5.3.

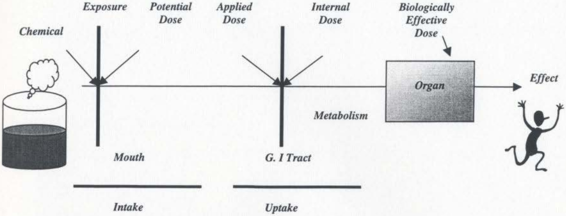


Figure 5.3. A schematic of dose and exposure (modified after U.S. EPA, 1992b)

In the current study the potential dose to the receptor was used for risk and potential effect estimates. The calculation for receptor dose was based on the following relationship.

$$CDI = \frac{(IR \times C \times EF \times ED)}{(BW \times AT)} \qquad (5.1)$$

where

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

IR = Intake rate (mg/day);

C = Pollutant concentration (mg/kg of fish);

BW = Body weight (kg);

AT = Averaging time (days);

EF = Exposure frequency (day/yr); and

ED = Exposure duration (yr)

The above equation determines the average daily dose of a chemical or a risk agent, per unit body weight, that a potential receptor may be exposed to over its life time (Sadiq et al., 20001e).

5.3.3. TOXICITY ASSESSMENT

The toxicity assessment uses dose response relationships to estimate the adverse health effects. The output of the assessment is used in risk calculations. The chemicals are generally categorized as potential carcinogens and non-carcinogens. The carcinogens receive more public attention generally. The mathematical relationships and computational methods of carcinogenic and non-carcinogenic effects are different. The dose response relationships for carcinogens are reported in the form of slope factors. It is a 95% upper confidence limit of the cancer on the dose-response curve and is expressed in $(mg/kg\text{-}day)^{-1}$. The non-carcinogens are expressed by their threshold values, reference dose (*RfD*). It is a daily dose, which is believed not to cause any adverse effect. It plays the same role as *PNEC* criteria value in ecological risk assessment (Chapter 4).

5.3.4. RISK CHARACTERIZATION

The fourth and the most important step in the human health risk assessment is the characterization of risk. The risk characterization includes quantitative estimates of both carcinogenic and non-carcinogenic risks. Risks are generally categorized for different exposure routes including ingestion, inhalation and dermal contact. In this study, the oral ingestion route is the only exposure pathway for which risks can be characterized.

Cancer Risk Model

Carcinogenic risk is a product of the chronic daily intake (*CDI*) and the carcinogenic slope factor (*SF*). This risk is the excess lifetime cancer risk from exposure to any particular chemical. The traditional methodology for risk assessment assumes additivity of risks from individual toxicants. Total carcinogenic risk is the summation of all exposure routes and for all contaminants. The excess lifetime risk can be calculated as

$$R_i = Risk = CDI \times SF \tag{5.2}$$

where,

CDI = Chronic daily intake (mg/kg-day); and

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

The conventional approach for estimating risks using input variables either using

1. mean values only;
2. regulatory defaults, in combination with mean values for parameters that are uncertain and for inter-individual variability, upper bounds (95th percentile) or with 5th percentile values when parameters are in denominator; and
3. upper bounds exclusively for all parameters.

When the mean values of input parameters are used it is called a "best estimate" ($\hat{R}_E$). When the 95th (and/or 5th %) values are used in risk assessment, it is called an estimate of "reasonably maximum exposed" person ($\hat{R}_{RME}$), and the third case corresponds to an upper conservative bound, ($\hat{R}_{High}$). The reasonably maximum exposed person estimate, $\hat{R}_{RME}$ is considered a conservative estimate of risk (i.e. above average) but not a worst-possible case (U.S. EPA, 1989, 1991; U.S. DOE, 1999).

Non-cancer Risk Model

Non-carcinogenic risk is generally characterized in terms of a *hazard index*. The index is the ratio of estimated chronic daily intake (*CDI*) to safe reference dose (*RfD*) and is estimated by the following relationship.

$$HI = \frac{CDI}{RfD} \tag{5.3}$$

where,

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

RfD = Reference dose (mg/kg-day); and

HI = Hazard index

If the acceptable level of intake is equal to the reference dose, HI will be 1. An exposure to chemicals is typical for multiple non-carcinogens. The hazard index scores for all contaminants are summed to provide the final measure of the risk for non-carcinogenic toxic effects. The target is that the summation of all indices should be less than 1 for the safe dose. If the mechanisms of toxic action of different non-carcinogens are well known, it is preferable to sum the hazard indices on an organ specific basis, e.g., if one contaminant is affecting the brain and another is affecting the kidneys, their effects are not generally summed up to get a total *HI*. However in this study, to simplify the problem the *HI* was grouped on the basis of number of exposure pathways and number of risk agents.

$$HI_c = \sum_{j=1}^{n} \sum_{i=1}^{m} HI \tag{5.4}$$

where

i to m = number of exposure pathways;

j to n = number of risk agents; and

HI_c = Composite *HI*

Risk can be obtained from *HI* as a non-dimensional probability of the hazard index exceeding unity (Maxwell and Kastenberg, 1999). The risk to an individual can be expressed in terms of probability of exceedence as given below:

$$Risk = p\,(\,HI_c \geq 1\,) \tag{5.5}$$

Background Risk

When the risks are characterized from exposure involving contaminants, an important consideration could be whether to include or exclude the background levels of the contaminants. The background level risks are important in deciding what maximum level of contamination is acceptable to protect the aquatic life. For drilling waste the background level concentration in the seawater of the heavy metals is more than the concentration in the water column due to the waste. But in comparison to pore water concentration the background levels are too low to cause a significant change in risk estimates.

Iterative Process in Risk Estimation

Risk assessment is an iterative process. The steps involved in the risk assessment process need assumptions due to unavailability of data and missing information. Therefore the sensitivities in the magnitude of the calculated risk should be quantified with other possible assumptions as well.

Uncertainties in Risk Estimation

For quantitative risk assessment, the uncertainty is an integral part of the calculations, but generally when risk estimates are reported, associated uncertainty is not reported. The quantitative methods used in different steps of human health risk assessment introduce a high degree of uncertainty and might raise questions as to the validity of the results.

Exposure assessment on future conditions is based on fate and transport modeling tools. The model structure and input variables may introduce uncertainty into the predictions. The toxicity assessment stage is a source of the highest uncertainty in the quantitative human health risk assessment, which is associated with slope factors and reference doses. For most of the contaminants, these values are not available, but even where data exist, extrapolation from animal tests is performed from values as high as 10-90% to 0.0001%

risk, through models. These extrapolations impair the accuracy of values. The computation of risk is the final stage, which is the measure of probability of rare events. It is not possible to calculate every conceivable outcome. To entertain various types of uncertainties, most of the time worst-case exposure scenarios are used for human health risk assessment. This brings inherent conservatism into calculations and could possibly include events that will never be experienced (LaGrega et al., 1994).

5.3.5. RISK COMMUNICATION

After characterizing the risk of exposure to contaminants and their associated uncertainties, this information is used in decision-making. This generally involves the public or at least public concerns and their response. Risk communications deal with identifying the "*level of acceptability of risk*" and "*risk perception*". The U.S. EPA has defined acceptable risk as one in a million (10^{-6}) to 1 in ten thousand (10^{-4}) for cancer and *HI* less than 1 for non-cancer risk. Risk perception means the acceptability and understanding of risk to the general public. For the drilling waste case, the contamination of fish may not be very high, but it is the involuntary risk to which people are exposed that is important. Therefore its quantification becomes an important issue.

5.4. U.S. EPA STUDY - HUMAN HEALTH RISK ASSESSMENT

The U.S. EPA (1999b) has estimated human health risk associated with consumption of finfish and shrimps for various scenarios of discharge. The analysis was performed for those contaminants for which bioconcentration factors (*BCFs*), oral reference dose (*RfD*) and/or oral slope factors (*SF*) for carcinogenic risk have been established. This analysis considered barite and formation oil as the source of contamination but did not consider synthetic base fluid itself due to unavailability of *RfDs* and *SFs* data (U.S. EPA. 1999b).

The U.S. EPA (1999b) used the results of a study by Brandsma (1996) to predict the effective concentration to which finfish are exposed in the water column. Instead of predicting concentration at 100 m (regulatory boundary for mixing), the environmental concentration was predicted at various distances within the mixing zone. The arithmetic mean of the environmental concentration was used further in the human health risk assessment. The mean predicted environmental concentration was divided by the number of dilutions (*DF*) available within 100 m. to calculate the effective exposure concentration for finfish. The effective environmental pollutant concentration (mg/L) was multiplied by the bioconcentration factor (*BCF*) of contaminants to estimate the concentration in finfish tissues. The estimated tissue concentration was then used as the human exposure concentration for calculating *HI* and risk. The following equations were used to estimate the contaminant concentration in fish tissues:

$$\text{Mean environmental concentration} = C_{mean} = \frac{C_{t1} + C_{t2} + ... + C_{tn}}{n} \tag{5.6}$$

$$\text{Effective finfish exposure concentration} = C_{ffe} = C_{mean} \times DF \tag{5.7}$$

$$\text{Human exposure concentrations} = C_{tissue} = C_{ffe} \times BCF \tag{5.8}$$

The following values for input parameters were used in the human health risk assessment:

FIR = Fish intake rate (99th percentile in California) = 177 (g/day);

C_{tissue} (mg/kg of fish)= Human exposure concentration;

BW = Body weight = 70 kg;

AT (days) = Averaging lifetime exposure = 70 × 365;

EF (days/yr) = Exposure frequency = 365; and

ED (yr) = Exposure duration = 30 and 70 (for two different exposure scenarios)

To calculate the pore water exposure concentration, the U.S. EPA (1999b) relied on a regression model based on a seabed survey, and developed a relationship of exposure concentration (mg/kg of sediment) as a function of distance. The average exposure concentration was then converted into shrimp tissue concentration by multiplying the average exposure concentration by the leaching factor (*LF*), *BCF* and lipid content (*Lc*) of the shrimps and then adjusted for density. In this analysis the deterministic input variables are used to estimate cancer and non-cancer risks.

In another study by the U.S. Department of Energy (U.S. DOE), Meinhold et al. (1996) estimated the human health risks in Louisiana Bay due to produced water discharges. Uncertainty analyses using Monte Carlo (MC) simulations were performed. Exposure and response parameters were defined with appropriate probability density functions. Radium (Ra) and lead (Pb) adverse effects were studied and concentrations in commercial fish were calculated based on their bioaccumulation potential. The input variables including dilution factor (*DF*), bioaccumulation coefficient (K_{ow}), and fish ingestion rates (*FIR*) were defined by uncertain input parameters. The incorporation of uncertainty in input parameters determines the uncertainty in human cancer and non-cancer risk estimation.

5.5. HUMAN HEALTH RISK ASSESSMENT PARAMETERS

The input parameters used in the human health risk assessment include exposure concentration, bioconcentration factor, lipid content of fish, intake rate, exposure frequency and duration, average body weight and average exposure time. The pore water exposure concentration is calculated from fate modeling (Chapter 3) which is then converted into fish tissue concentration by the following relationship:

$$\mathit{Fish\ tissue\ concentration} = \mathit{Exposure\ concentration} \times BCF \times \mathit{Lipid\ content}\ (Lc) \qquad (5.9)$$

(mg/kg of fish) (mg/L) (L/kg of fish fat) (kg of fish fat/kg of fish)

The fish tissue concentration is then used in equation 5.1 to calculate the chronic daily intake (*CDI*). The details of risk assessment input parameters are given in the subsequent sections.

5.5.1. BIOCONCENTRATION FACTOR (*BCF*)

The bioconcentration factor is the ratio of concentration in organism tissue (mg/kg) to the concentration in water (mg/L). Bioconcentration factor (*BCF*) values are selected from empirical field and/or laboratory data generated from peer reviewed studies that are published in the scientific literature. If two or more *BCF* values are available, or two or more sets of collocated data are available, the geometric mean is used (U.S. EPA, 1999d).

Generally *BCF* values estimated from field studies are given more weight and considered more indicative of the natural environment than the laboratory studies. These field studies values are defined as 'recommended *BCF* values'. Sometimes laboratory-derived values are recommended when confidence in reported field values is less. When an appropriate surrogate is not identified, regression equation based on chemical $LogK_{ow}$ is used to calculate the 'recommended *BCF* values'.

The *BCF* values for various heavy metals are reported in Table 5.3. The values are collected from various key sources including Thompson et al. (1972), Saiki et al. (1995), and U.S. EPA (1992c, 1999b). The *BCF* values are reported for different species of finfish and shellfish in seawater and freshwater. The reported values for different fish species are assumed to be valid for the marine environment under study.

5.5.2. FISH INGESTION RATE (*FIR*)

Contaminated fish is a potential source of human exposure to toxic chemicals. Pollutants enter into surface waters and accumulate in sediments and biota due to their affinity towards organic matter through complex physico-chemical processes. To estimate the human exposure of toxic chemicals, fish ingestion rates (*FIR*) are determined for a potential exposed population. Commercially caught fish are marketed widely and exposure to the general public is difficult to estimate (U. S. EPA, 1997). The U.S. EPA (1999b) used a conservative approach and assumed *FIR* as the highest 99th percentile value (i.e., 177 g/day) from human consumption data in California.

Table 5.3. Water-to-fish bioconcentration factor (*BCF*) values

Metal	Reference	*BCF* (L/kg)	
		Values	Recommended
As	Thompson et al. (1972)	333 100	114
	U.S. EPA (1992c); U.S. EPA (1999b)	44	
Cd	Saiki et al. (1995)	558 1295 729 1286	907
	Benoit et al. (1976)	716	
	Eisler et al. (1972)	480	
	Harrison and Klaverkamp (1989)	161 51	
	Kumada et al. (1980)	33	
	Kumada et al. (1973)	8 3333	
	Spehar (1976)	4.4	
	Thompson et al. (1972)	3000 200	
	Williams and Giesy (1979)	4100	
	U.S. EPA (1999b)	64	
Cr (Total)	Williams and Giesy (1979)	1.27 1.34	19
	Thompson et al. (1972)	200 400	
	U.S. EPA (1999b)	16	
Hg	Boudou and Ribeyre (1984)	1800	3530
	Snarski and Olson (1982)	4380 5580	
	U.S. EPA (1999b)	5500	

Table 5.3. Water-to-fish bioconcentration factor (*BCF*) values (Contd.)

Metal	Reference	*BCF* (L/kg)	
		Values	Recommended
Ni	Thompson et al. (1972)	100 100	78
	U.S. EPA (1992c); U.S. EPA (1999b)	47	
Zn	Saiki et al. (1995)	2299 2265 4290 804	2059
	Deutch et al. (1980)	50 130 130 200	
	Pentreath (1973)	373 8853	
	Thompson et al. (1972)	1000 2000 2000	
	U.S. EPA (1992c)	47	
Naphthalene	Howard (1989)	40 - 1000	426
	U.S. EPA (1999b)	426	

Meinhold et al. (1996) have derived ingestion rates from reported data on a meals per week basis for recreational fishermen at Louisiana Bay. They have reported the ingestion rates for two types of population including (i) recreational fishermen and their families and (ii) children. Table 5.4 summarizes the values used in this study.

The U.S. EPA's exposure factor handbook (1997) reports the fish ingestion rates for various types of fish for various exposed populations. Survey data on fish consumption were collected using different approaches, which included telephone and mail surveys, personal interviews and diary and creel surveys. Table 5.5 summarizes the results of *FIR* values for the general public. The results of 50th and 95th percentile *FIR* values with 90th bootstrap intervals (*BI*) are listed. For the mean value instead of *BI*, the confidence interval (*CI*) is reported. Marine fish ingestion rates are reported either as *uncooked* or *as consumed*. The "*uncooked*" values are reported in g/day and "*as consumed*" in mg/kg-day. The 95th percentile of "*as consumed*" (3.888 mg/kg·day) with a 90th percentile interval of 3.771 - 4.113 mg/kg·day are used in this analysis. The advantage of using fish mass ingested per unit body weight is that body weight (*BW*) and fish ingestion rate (*FIR*) may be correlated. If these parameters are used as independent variables in the analysis, this might lead to erroneous risk estimations. In the absence of a reliable correlation coefficient, it is preferred to use fish dosage per unit body weight as a single parameter in human health risk assessment.

Table 5.4. Fish intake rate caught at open bay platform

(modified after Meinhold et al., 1996)

Statistics	Recreational fishermen and families (g/day)	Children (g/day)
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

Table 5.5. Fish intake rate caught at open bay platform (mg/kg-day)

Category/Comments	Estimate	Values	Interval	Values
Marine (Finfish and shellfish) (g/day - uncooked)	50th percentile	93	90th *BI*	108 - 118
	95th percentile	272	90th *BI*	261 - 280
Marine (Finfish and shellfish) (mg/kg-day - uncooked)	50th percentile	1.927	90th *BI*	1.830 - 2.024
	95th percentile	5.019	90th *BI*	4.852 - 5.267
Marine (Finfish and shellfish) (g/day - as consumed)	50th percentile	88	90th *BI*	84 - 92
	95th percentile	209	90th *BI*	198 - 222
Marine (Finfish and shellfish) (mg/kg-day - as consumed)	mean	1.495	90th *CI*	1.423 - 1.568
	95th percentile	3.888	90th *BI*	3.771 - 4.113

The U.S. EPA (1997) has also provided a checklist for establishing authenticity and validity of the results reported in Table 5.5. The reported values are derived from sample sizes ranging from 10.000 to 37.000 people. The reported data are collected from mid and south Atlantic regions. Table 5.6 summarizes these considerations and rates the confidence of reported values. The overall ranking of confidence of the reported value is medium to high as shown in Table 5.6.

5.5.3. LIPID CONTENT (*Lc*)

The fat or lipid content present in fish may vary from one species to another. The toxic chemicals attach themselves to the fat present in the biota. The U.S. EPA (1999b) has used 1.1% *Lc* for shrimps for calculating exposure concentration through drilling waste discharges for human consumption. The U.S. EPA (1997) has reported lipid or fat content values for various marine species of finfish and shellfish. Table 5.7 summarizes lipid content of some of these important marine species.

Table 5.6. Confidence in fish intakes for general population (after U.S. EPA. 1997)

Considerations	Rationale	Rating
Level of peer review	Peer reviewed by U.S. DOE and U.S. EPA	High
Accessibility	In public domain	High
Reproducibility	Enough information is available to reproduce results	High
Focus on factor of interest	The study focussed on fish ingestion	High
Data pertinent to Newfoundland	Data includes Atlantic regions as well	Medium
Study size	Sample size vary from 10, 000 to 37,000	High
Lack of bias in study design	Response rates are fairly high	High
Measurement error	Estimates of measurements are imprecise	Medium
Overall ranking		Medium to High

5.5.4. EXPOSURE DURATION (*ED*)

The exposure duration (*ED*) denotes household residence time in that city or place that would be supplied with contaminated fish. The U.S. EPA (1999b) used two exposure scenarios in the analysis: 30 and 70 years.

According to U.S. DOE (1999), *ED* accounts for households moving into and out of that area, and is generally modeled through joint uncertainty and interindividual variability (*JUV*). The U.S. DOE (1999) has reported values of the *ED* for risk estimation for "best estimate" ($\hat{R}_E$). estimate of "reasonably maximum exposed" person ($\hat{R}_{RME}$). and for upper conservative bound. ($\hat{R}_{High}$). The values are defined in Table 5.8.

Table 5.7. Lipid content (*Lc*) of selected finfish/shellfish species
(modified after U.S. EPA, 1997)

Species	Lipid content (*Lc*) (%)	Comments
Cod, Atlantic	0.46 0.58 1.61	Raw Canned Dried
Croaker, Atlantic	2.70 11.71	Raw Cooked
Flounder	0.81 1.08	Raw Cooked
Haddock	0.49	Raw
Mullet, Striped	2.91	Raw
Ocean Perch, Atlantic	1.30	Raw
Salmon, Pink	2.85	Raw
Salmon, Red	4.56	Raw
Sardine, Atlantic	10.55	Canned in oil
Shrimps, Mixed Species	1.25	Raw
Mussel, Blue	1.54	Raw
Squid	0.99	Raw

5.5.5. AVERAGING TIME (*AT*)

The averaging time is generally taken as 70 years (U.S. EPA, 1999b; U.S. DOE, 1999). According to Statistics Canada (2001) the expected average life in various provinces of

Canada is reported in Table 5.9. These statistics represent the age census data for years 1990 to 1992. The overall average expectancy of life (*AT*) for both sexes is 77 years for the Newfoundland population. The U.S. DOE (1999) has also recommended *AT* as a point estimate in human health risk calculations.

Table 5.8. Exposure duration (*ED*) in years for various types of risk estimates (U.S. DOE, 1999)

$\dot{R}_{E}$	$\grave{R}_{RME}$	$\grave{R}_{High}$
7.6 U.S. DOE (1999) - The number of years an individual residing at the impacted site in the span of 70 years lifetime.	30 Regulatory values reported by U.S. EPA (1999b) and U.S. DOE (1999).	55.3 Approximation for 95th percentile for upper bound of exposure distribution. The procedure used to obtain *ED* distributions adapts the Israeli and Nelson (1992) model of variability in the time of residence for households.

5.5.6. EXPOSURE FREQUENCY (*EF*)

The U.S. EPA has reported an exposure frequency (*EF*) of 365 days/yr for human health risk assessment, whereas the U.S. DOE (1999) has recommended an *EF* of 350 days/yr for regulatory purposes in human health risk assessment. Both studies used *EF* as a point estimate in the risk assessment calculations

Table 5.9. Averaging time (*AT*) in years for various provinces in Canada
(Statistics Canada, 2001)

Province or State	Both sexes	Male	Female
Newfoundland (NF)	**77***	74	80
Prince Edward Island (PEI)	77	73	81
Nova Scotia (NS)	77	74	80
New Brunswick (NB)	78	74	81
Quebec (QB)	77	74	81
Ontario (ON)	78	75	81
Manitoba (MB)	78	75	81
Saskatchewan (SK)	78	75	82
Alberta (AB)	78	75	81
British Columbia (BC)	78	75	81

* 28.105 days

5.5.7. SUMMARY OF INPUT PARAMETERS

Table 5.10 summarizes the proposed design values of various HHRA input parameters and also compares them with regulatory values. The minimum, most likely and maximum are reported in proposed design values. The most likely value (MLV) is defined based on either recommended values or most quoted values. The point estimates of averaging time (*AT*) and exposure frequency (*EF*) are reported. The maximum value of lipid content (*Lc*) for some species are more than 10% but most reported values have *Lc* less than 5% and this is taken as the maximum value.

Table 5.10. Proposed parameters for human health risk assessment (HHRA)

Parameter (type)	*Proposed values	Regulatory values		
		U.S. DOE (1999)	U.S. EPA (1999b)	U.S. EPA (1999d)
BCF (L/kg) (variability)	As: (44, 114, 333)		44	114
	Cd: (4.4, 907, 4100)		64	907
	Cr: (1.27, 19, 400)		16	19
	Hg: (1800, 3530, 5580)		5.500	3530
	Ni: (47, 78, 100)		47	78
	Zn: (47, 2059, 8853)		47	2059
	Naphthalene: (40, 426, 1000)		426	
FIR (mg/kg-day) (as consumed) (variability)	(3771, 3888, 4113) 95th percentile at 90% BI	95th percentile	Used 99th percentile, i.e., 177g/day	
Lc (%) (variability)	(0.4, 1.1, 5) Generally 5% as maximum value, is reported.		1.1	
ED (yr) (Not applicable)	(7.6, 30, 55.3)	95th percentile 55.3	30 and 70	
EF (day/yr) (not applicable)	350	350	365	
AT (days) (Not applicable)	28,105 Based on local census values	25.550	25.550	
C (mg/L) (uncertainty) concentration in media	Based on 95th percentile, exposure concentration regression model in Chapter 3. The 90% *CI* is used as lower and upper bound.	95th percentile	Mean	90th percentile is recommended by Lenwood et al. (1998)

*(minimum, most likely or mode, maximum)

5.6. PROPOSED METHODOLOGY

Because of simplifying assumptions and the imprecise nature of available information, human health risk assessments are prone to uncertainty. The uncertainty is inherent to risk and an integral part of risk assessment. In human health, the risk is often defined as the probability that damage or adverse effects may occur. Human health risk assessment models consider uncertainties associated with the exposure of the receptor to the contaminants emitted from the source. The other type of uncertainty is related to input parameters. The uncertainties are generally estimated with the help of Monte Carlo (MC) simulations or a fuzzy based approach (Guyonnet et al., 2000).

The MC method assumes that model parameters are random variables and are represented by probability density functions (PDFs). The basis for MC simulation is quite simple in that point estimates are replaced by PDFs and samples are taken randomly from each distribution. The output of the model is also in the form of a PDF or CDF (cumulative distribution function). The MC simulations have been explained in detail in Chapter 3.

Fuzzy arithmetic is a generalized form of interval analysis, which also addresses uncertainty. Instead of representing a number with a single interval or range, it uses a fuzzy number, a group of intervals stacked on top of each other to represent an estimate of the uncertainty. Fuzzy arithmetic is a very useful way to propagate uncertainty because it covers both worst case results and best estimates at the same time. Fuzzy arithmetic is appropriate for handling non-statistical uncertainty including that due to the inability to make accurate measurements. The methodology is computationally fast and does not need extensive sampling (Ferson, 1996).

The framework for treating vague or imprecise information was introduced by Zadeh (1965). In the fuzzy approach, instead of representing uncertainty with PDFs, fuzzy numbers are allotted to variables. A fuzzy number describes the relationship between an uncertain quantity X and a membership function μ_A. This function is comprised of a range between 0 and 1. Any shape of fuzzy number is possible, but the selected shape should be justified by available information. The basic difference between PDFs and fuzzy numbers is that the area under PDFs is equal to 1, which is not valid for a fuzzy number. In recent years fuzzy arithmetic applications in environmental problems have increased. Dou et al. (1995), Bardossy et al. (1995) and Guyonnet et al. (2000) are a few examples of fuzzy calculus in environmental engineering.

To maintain consistency with the methodologies developed in preceding chapters, MC simulations were used for performing human health risk assessment. The following steps were followed for conducting human health risk assessment:

- The MC simulations using Latin Hypercube Sampling was proposed for human health risk assessment. The parameters of the cancer and non-cancer risk models were defined by simple triangular probability density functions (PDF).

- The equation for *CDI* was modified as given below. The minimum, most likely (MLV or mode) and maximum values were defined for each input parameter (Table 5.11).

$$CDI = \left(\frac{FIR \cdot (C \cdot 10^{-6} \cdot BCF \cdot Lc) \cdot EF \cdot ED}{AT} \right) \tag{5.10}$$

where

CDI = Chronic daily intake (mg of contaminant/kg of human body weight/day);

FIR = Fish ingestion rate (mg of fish/kg of human body weight-day);

C = Pollutant concentration (mg of contaminant/L of water);

AT = Averaging time (days);

EF = Exposure frequency (day/yr);

ED = Exposure duration (yr);

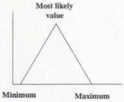
10^{-6} = Unit conversion (kg/mg);

Lc = lipid content (fat fraction); and

BCF = Bioconcentration factor (L/kg)

- The estimated *CDI* was used to determine the cancer and non-cancer risk as given in equations 5.2 to 5.5. The *RfDs* and *SFs* for risk agents are point estimates and uncertainties in their estimates are not reported. The output of cancer risk and non-cancer risk models were in the form of EDFs. The *HI* was summed up for all risk agents to obtain HI_c as a risk estimate for non-cancer hazard.

Table 5.11. Triangular distributions for human health risk assessment input parameters

Parameters	Triangular distribution			Shape
	Minimum	MLV	Maximum	
FIR (mg/kg·day)	3,771	3,888	4,113	
BCF (L/kg)	Based on Table 5.10. Minimum and maximum values are taken from available data. The most likely value is defined based on the regulatory recommended value.			
Lc (%)	0.4	1.1	5.0	
ED (yr)	7.6	30	55.3	
EF (days/yr)	350			
AT (days)	28,105			
C (mg/L) 95th percentile exposure concentration. The adjusted value of predicted environmental concentration for bioavailable fraction (*BF*) and probability of exposure.				

The framework of human health risk assessment methodology for cancer and non-cancer risk agents is shown in Figure 5.4. This framework summarizes the steps that are discussed in the proposed methodology for human health risk assessment. The pollutant concentrations estimated from regression models were used as the exposure concentration for the commercial fish. This exposure concentration was used to estimate pollutant concentrations in fish tissues. The fish tissue concentration was used in estimating the chronic daily intake for cancer and non-cancer risk estimates.

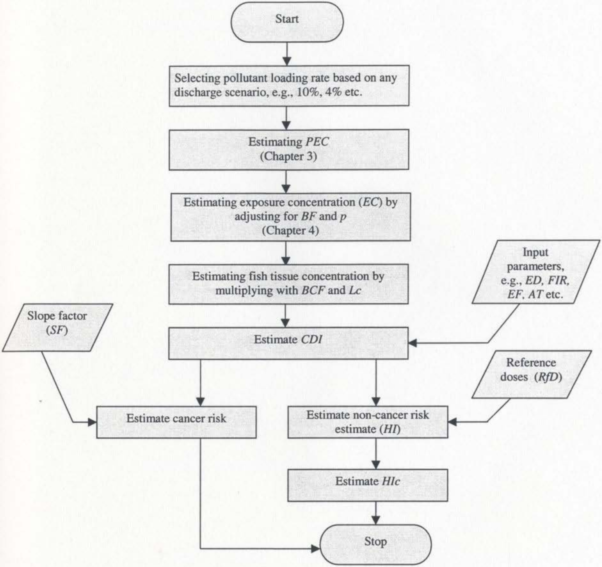


Figure 5.4. A proposed framework for conducting human health risk assessment

The human health cancer and no-cancer risk estimates can be combined with the ecological risk (Chapter 4) to determine the total environmental risk for any given drilling waste discharge scenario. The methodology for combining risk estimates for environmental risk management is discussed in the next chapter.

Chapter 6

RISK MANAGEMENT

Risk management is an integral part of ecological and human health risk assessments as discussed in Chapters 4 and 5, respectively. Risk management explores and evaluates various alternatives and options which can optimise the risk posed by natural and anthropological activities at minimum cost and resources.

6.1. INTRODUCTION

The major objective of risk management is to help in decision-making and selection of the best alternative available, which can reduce the risk at minimal cost. The application of risk management tools aid in the selection of prudent, technically feasible and scientifically justifiable actions that will protect the environment and human health in a cost-effective way. Risk management is a process of weighting alternatives and selecting the most appropriate action, integrating the results of risk assessment with engineering data and with social, economic, and political concerns to reach a decision.

Risk management integrates political, legal and engineering approaches to manage risks. Risk management is the action proposed based on the best alternative from the decision-maker's point of view and individual/group priorities. Generally risk assessment is carried out objectively, whereas risk management involves preferences and attitudes, which have objective and subjective elements (Duah, 1993).

This chapter first describes various multiple criteria or multiple attribute decision-making (MCDM or MADM) approaches, which are commonly used in environmental risk management. These approaches are discussed with the help of fuzzy logic concepts. In addition to MCDM, various alternative ranking techniques and weighting schemes are discussed. The proposed MCDM approach - fuzzy composite programming involving the analytical hierarchy process (AHP) and weighting schemes are discussed in detail. Secondly the cost estimation for environmental damage and treatment technologies, and the status of various treatment options are described. Only those treatment technology options that are relevant to offshore disposal of drilling waste are discussed in this chapter. In the end, the research methodology developed in Chapters 2 to 6 is summarised. This overall research summary will help in applying the developed methodology for a case study in Chapter 7. Figure 6.1 illustrates and explains the organisation of this chapter.

6.2. MULTIPLE CRITERIA DECISION-MAKING (MCDM)

Decision-making is an integral part of all management issues and is part of our daily lives. The main concern in decision-making is that decision problems are multiple and diverse in nature and usually have conflicting criteria. In the last 30 years, research related to multiple criteria decision-making (MCDM) or multiple attribute decision-making (MADM) has produced enormous literature in the fields of engineering, business and social sciences. Decision-making is broadly classified into MCDM and MODM (multiple objective decision making). The MCDM is associated with problems whose alternatives are predefined and the decision-maker is to select or rank various alternatives. The MODM designs the most promising alternative with respect to limited resources. Hwang and Yoon (1981) have critically reviewed methods and applications of MCDM/MODM for a single decision-maker. For more than one decision-maker, the problem becomes complex and the best solution is the one that will be accepted by all decision-makers. Hwang and Lin (1987) have also discussed group decision-making under multiple criteria.

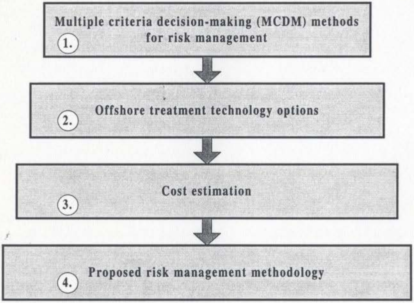


Figure 6.1. Organization of chapter for developing a methodology for risk management

Fuzzy set applications in decision-making are the extension of many methods used in crisp sets of multiple criteria techniques. Chen and Hwang (1992) have summarised various MCDM methods and categorised them. Research attempts to incorporate uncertainty into decision-making of various attributes involve probability theory and/or fuzzy set theory. Fuzzy set theory is an important tool for modeling uncertainty or imprecision arising from human perception. Human judgement is involved in decision making in different disciplines, therefore a rational approach toward decision making has to take into account human subjectivity.

A MCDM problem can be expressed in a matrix form

$$\begin{array}{c} \\ \mathbf{A_1} \\ \mathbf{A_2} \\ \cdot \\ \cdot \\ \mathbf{A_m} \end{array} \begin{array}{c} \begin{array}{ccccc} \mathbf{X_1} & \mathbf{X_2} & \cdot & \cdot & \mathbf{X_n} \end{array} \\ \left[\begin{array}{ccccc} X_{11} & X_{12} & \cdot & \cdot & X_{1n} \\ X_{21} & X_{22} & \cdot & \cdot & X_{2n} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ X_{m1} & X_{m2} & \cdot & \cdot & X_{mn} \end{array} \right] \end{array} \tag{6.1}$$

where

$A_i = 1, 2, \ldots, m$ are possible courses of action or alternatives;

$X_j = 1, 2, \ldots, n$ are attributes with reference to measured alternative performances; and

X_{ij} = Performance or rating of alternative A_i with respect to attribute or criteria X_j.

In practical problems, it is common that X_{ij} are not assessed precisely due to unquantifiable, incomplete and non-obtainable information and partial ignorance. The unquantifiable information leads to subjective attributes, for example good, poor, high, low, etc. Examples of incomplete information are "about one million", " less than 10 miles per hour" etc. Sometimes crisp data are obtainable but need a lot of resources, but "approximation" is possible with less effort and time. Sometimes linguistic descriptions are used because of non-availability of information. Fuzziness is also attributed due to ignorance of factual conditions. These limitations in MCDM methods lead to fuzzy based approaches.

6.2.1. CLASSIFICATION OF FUZZY MCDM METHODS

A basic introduction to fuzzy numbers is given in Chapter 5. The applications of fuzzy set theory in various engineering disciplines, especially in decision-making, have gained a lot of popularity. To perform MCDM using fuzzy based methods, the following two steps are followed:

- The aggregation of the performance scores with respect to all the attributes for each alternative; and

- The rank ordering of the alternative according to the aggregated scores

These two steps are referred to as "final rating" and ranking order", respectively. In crisp MCDM the final rating is expressed in real numbers, therefore rating order can easily be explained. Therefore, in traditional crisp MCDM only the first step is relevant. In a fuzzy MCDM problem, the performance scores of the alternatives are compared and the rank order of fuzzy numbers is determined, which is not a trivial task. Therefore, both phases are integral parts of fuzzy MCDM. The taxonomy of fuzzy MCDM methods is shown in Figure 6.2. Chen and Hwang (1992) have classified MCDM models based on the following four stages:

1. Problem size;
2. Data type;
3. MCDM methods; and
4. Techniques.

The size of the MCDM problem depends on the size of alternatives and attributes. Generally, fuzzy methods are suitable for alternatives and attributes less than 10. The data could be in the form of (1) all fuzzy, (2) all fuzzy singleton (single value and its corresponding membership function), (3) all crisp, and mixture of fuzzy and crisp. In stage 3, the concepts of fuzzy methods are derived from classical methods of MCDM: simple additive weighting (SAW), analytical hierarchy process (AHP), multiple attribute utility function (MAUF), etc. This final stage provides the techniques required for applying fuzzy MCDM methods that include the α-cut method, fuzzy arithmetic operations, possibility and necessity measures, eigen-vector method, etc. The details of references and sources of these approaches can be seen in Chen and Hwang (1992).

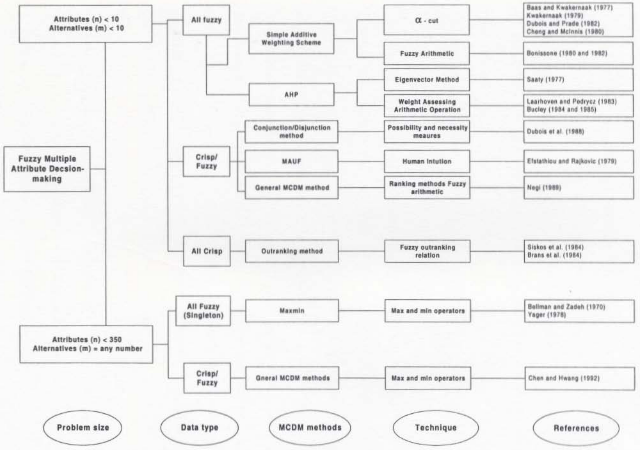


Figure 6.2. A taxonomy of fuzzy MCDM methods (Chen and Hwang, 1992)

6.2.2. FUZZY COMPOSITE PROGRAMMING (CP) FOR DECISION-MAKING

Fuzzy composite and compromise programming techniques are not given in the taxonomy provided by Chen and Hwang (1992). Fuzzy composite programming is an extension of compromise programming (Bogardi and Bardossy. 1983). In this approach. the analytical hierarchy process and fuzzy arithmetic are used. Recently. this approach has gained popularity and many researchers have used it in environmental decision-making problems (e.g., James and Lee. 1992; Lee. 1992; Lee et al., 1991 and Stansbury et al., 1989 etc.). A detailed description of this technique is given in this section.

It is difficult to select an appropriate risk management strategy when the values of input variables. such as ecological and human health risks. cost. and qualitative terms like technical feasibility. are uncertain. Some multiple criteria decision-making optimization tools. including linear multi-objective programming. goal programming. compromise programming. composite programming. multi-attribute utility theory and ELECTRE programming are very popular for this type of problem. Stansbury (1991) has compared some of the decision-making models including MAUF. ELECTRE and composite programming (CP) and suggested that the choice of an appropriate MCDM method depends on the following factors:

1. Type of attribute values - qualitative or quantitative.
2. Types of alternatives - continuous or discrete options.
3. Robustness of results with respect to changes in attribute values.
4. Ease of computation. and

5. Decision-maker - an individual or a group.

Compromise programming, composite programming, and multi attribute utility theory can effectively deal with discrete and continuous options. These MCDM tools are used to assist decision-makers in solving problems involving multiple attributes and multiple criteria. The uncertainties inherent in these problems are often treated separately from the decision process itself. The decision analysis is often carried out using point or crisp estimates, meaning no uncertainty within input variables. Fuzzy composite programming (CP) is used to assist decision-makers in solving problems of multiple attributes and conflicting objectives. Lee (1992) and Lee et al. (1991) incorporated such uncertainties in MCDM processes for the management of dredged material disposal and for developing management strategies for nitrate control in drinking water.

Stansbury et al. (1989) have developed a methodology that uses composite programming for studying the risk-cost tradeoffs of dredged materials in terms of ecological, human health and socioeconomic impacts. The environmental risk and cost due to excavation, transportation, and disposal of dredged material were evaluated for different available alternatives. The objective was to consider both the economics of dredging and human-health and ecological risks that are associated with dredging processes. Basic indicators such as carcinogenic and non-carcinogenic human health risk, ecological risks and costs were defined. Composite programming (CP) organizes the problem into the following format:

1. Identification of management alternatives:
2. Definition of basic indicators:
3. Grouping them into more generalized indicators:
4. Defining weights. balancing factors. the best and worst values of the indicators: and
5. Estimation and ranking of the alternatives.

CP is a step by step procedure of regrouping a set of various basic indicators to form a single indicator (Bogardi and Bardossy. 1983). CP uses a composite structure of the basic indicators selected for risk management of drilling waste. In addition to cost and technical feasibility. risks to both human and non-human populations can also be taken as basic indicators. Carcinogenic and non-carcinogenic human health and ecological risks can also be considered.

The first step in CP is the normalization of the basic indicators. This is necessary because all basic indicators have different units and are difficult to compare in their respective units. At the first level. human cancer and non-cancer risks are determined for different contaminants. which are grouped into cancer and non-cancer human risk indices. Similarly. ecological risks for all species of commercial significance are determined for different contaminants to get ecological risk indices. At level 2. the human health cancer and non-cancer risks are grouped as a human health risk index. The same procedure is repeated for individual ecological risk indices to get a final ecological risk index. The Level-2 human and ecological risk indices are grouped to form the final environmental risk at Level 3. The same procedure is repeated for cost and technical feasibility of treatment operations. The grouping for different attributes is performed in steps, until we get the total risk index, total cost and total technical feasibility of operations to make a trade-off analysis among conflicting objectives. This trade-off analysis for different alternatives can be done at all hierarchy levels. The system index value at Level 4 represents the contribution of the final risk index, total cost and final technical feasibility of operations. Figure 6.3 shows a framework of composite programming in a step by step procedure for risk management of drilling waste discharges.

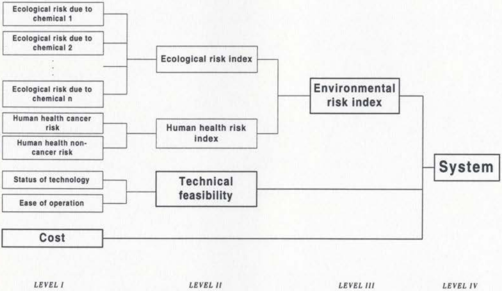
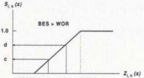


Figure 6.3. The framework for fuzzy composite programming for drilling waste risk management

A fuzzy set U is defined as a set of objects or elements x as U = $\{x\}$. Therefore a fuzzy set A in U is characterised by a set of ordered pairs A = $\{(x), \mu_A(x)\}$, $\forall$ U $\ni x$, where $\mu_A(x)$ is grade or degree of membership of x in A (Zadeh, 1965). The membership function $\mu_A(x)$ assumes its value [0, 1]. When $\mu = 0$, it does not belong to A and if $\mu = 1$, it indicates x is definitely an element in A. Values between 0 and 1 show the degree of belief.

The values of the basic indicators can be designated by fuzzy numbers to characterise their uncertainties. By defining $Z_i\ (x)$ as a fuzzy number of the i^{th} basic indicator with a trapezoidal membership function of $\mu[Z_i\ (x)]$, various management alternatives under uncertainty can be evaluated. The confidence level for an uncertain value can be determined using observed or measured variability. Since units of basic indicators are different, the actual value of each basic indicator should be transformed into an index, $S_{i,h}(x)$, using the best or the worst value of the indicator as shown in Figure 6.4 (Lee, 1992).



$$S_{i,h}(x)=\begin{bmatrix} 1 \\ \dfrac{Z_{i,h}(x)-WORZi}{BESZi-WORZi} \\ 0 \end{bmatrix} \begin{matrix} Z_{i,h(x)} \geq BESZi \\ WORZi < Z_{i,h}(x) < BESZi \\ Z_{i,h}(x) \geq WORZi \end{matrix}$$

$$S_{i,h}(x)=\begin{bmatrix} 1 \\ \dfrac{Z_{i,h}(x)-WORZi}{BESZi-WORZi} \\ 0 \end{bmatrix} \begin{matrix} Z_{i,h(x)} \leq BESZi \\ BESZi < Z_{i,h}(x) < WORZi \\ Z_{i,h}(x) \geq WORZi \end{matrix}$$

Figure 6.4. Transforming actual value $Z_{i,h}\ (x)$ into normalized index value $S_{i,h}\ (x)$

Using the index values of basic indicators, the Level 2 index values, $L_{j,h}\ (x)$, of composite indicators can be defined by

$$L_{j,h}(x) = \left\{ \sum_{i=1}^{nj} w_{i,j} \left[S_{i,h,j}(x) \right]^{pj} \right\}^{(1/pj)} \tag{6.2}$$

where,

$n_j =$ Number of elements in second-level group j;

$S_{i,h,j}(x) =$ Basic value for i^{th} basic indicator in the second level group j of basic indicators with membership of h;

$w_{i,j} =$ Weight reflecting the importance of each basic indicator ($\sum w_{i,j} = 1$); and

$p_j =$ The balancing factor for group j.

Further, the index values $L_{k,h}(x)$, of the third level composite indicators can be calculated by using the index values for the second level composite indicators. This procedure is repeated until the final step, which compares three index values of the 4th level indicators: environmental risk, cost and technical feasibility.

Selecting weights (w) and balancing factors (p) depends on a single or group of decision-makers. The weights represent the relative importance of each indicator as viewed by a decision-maker, whereas the balancing factors account for maximum deviation of the indicators and limit the ability of one indicator to substitute for another. A weighting technique is used to group basic indicators into more general groups. The weights are allotted in each group based on their relative importance. The process, called an analytical hierarchy process (AHP), is used to determine the weight of each indicator in a group by a paired comparison of each of the indicators (Saaty, 1988; Lee, 1992).

To determine the ranking for various management alternatives, assume $L(x)$ as a fuzzy number, which is represented by a final composite indicator of alternative x. With the help of two index values, $L_{h=1}(x)$ and $L_{h=0}(x)$, the membership function, $\mu[L(x)]$, of the fuzzy number can be calculated approximately. For m management alternatives there are m fuzzy numbers, $[L(x), x = 1, 2, \ldots, m]$, to which any ranking method can be applied. The Chen ranking method (1985) determines the ranking of m fuzzy numbers by using maximising and minimising sets. This method has been extensively used in ranking alternative studies (Lee, 1992; Stansbury, 1989). The methodology of fuzzy composite programming allows the incorporation of complex social, ecological and economic information into the fuzzy decision making process. The details of weighting schemes and fuzzy ranking methods are given in later sections.

6.2.3. CONVERTING LINGUISTIC TERMS TO FUZZY NUMBERS

In MCDM we generally deal with linguistic terms good, very poor, excellent etc. A numerical approximation is proposed to convert linguistic terms into corresponding fuzzy numbers. Chen and Hwang (1992) have defined eight scales to convert linguistic terms into fuzzy numbers. Two important scales are reported in Figure 6.5. The first scale has 3 levels, whereas the second scale contains five levels. The linguistic terms for the first scale are "low", medium" and "high". In the second scale, two additional degrees - "very low" and "very high" - are introduced.

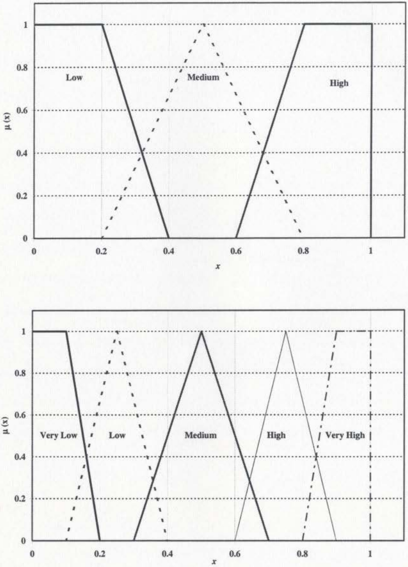


Figure 6.5. Conversion of linguistic terms into numerical scores

The same linguistic terms contain different meaning at different scales. The "high" in first scale means [(0.6,0), (0.8,1.0), (1.0,1.0), (1.0,0)], i.e. the most likely interval (when the membership function, μ is 1) is in between 0.8 and 1 and the largest likely interval is in between 0.6 and 1 (when the membership function, μ is 0). But in the second scale the "high" means [(0.6,0), (0.75,1.0), (0.9,0)]. This reflects the fact that the same linguistic terms may posses different meaning for different occasions.

The principle of this system is to pick a scale that contains all verbal terms given by the decision-maker and use the fuzzy numbers in that scale to represent the meaning of the verbal terms. Chen and Hwang (1992) have recommended that scales be used in the simplest form available. The determination of the number of conversion scales is intuitive. Miller (1965) has pointed out that " 7 ± 2 " represents the greatest amount of information that an observer can give about the objects based on absolute judgement. Therefore, the scales between 5 and 9 may contain maximum information about relative importance of options/alternatives, which are to be compared. In risk management of drilling waste some basic indicators are defined qualitatively. The scale shown in Figure 6.5 will help in defining the numerical scores for those basic indicators used in fuzzy composite programming.

6.2.4. FUZZY RANKING METHODS

In traditional MCDM methods, all X_{ij}, and W_j (relative importance of attributes) values are taken as crisp values. A utility function $U\ (x_1, x_2, \ldots, x_m)$ is defined by a decision-maker. For alternatives A_i, the utility function aggregates its performance ratings X_{ij} into a final rating, U_i. This final rating determines how well one alternative satisfies the decision-maker's utility. The alternatives with higher final ratings are preferred by a decision-maker. If the final ratings are real numbers, then it is straightforward to decide on the best alternative.

The alternative performance rating X_{ij} can be crisp, fuzzy, and/or linguistic. When fuzzy data are incorporated into MCDM problems the final ratings are no longer crisp numbers, rather they are fuzzy numbers. The fuzzy numbers are not straightforward to compare. In MCDM applications when the final ratings are fuzzy, different ranking methods can be used to compare these fuzzy utility values. Chen and Hwang (1992) have classified ranking methods into four major groups as shown in Figure 6.6.

These groups are preference relation, fuzzy mean and spread, fuzzy scoring and linguistic expression. Each class is further categorised based on the technique involved. Fuzzy scoring techniques are the most popular. In defining left/right scores, Chen's ranking method (1985) is extensively used for risk-cost trade-off analysis (e.g., Stansbury et al. (1989), Lee (1992) etc.). Another simple and popular method proposed by Yager (1980a, b) is based on centroid value. Details of Chen (1985) and Yager (1980a, b) methods are given in the next section.

Chen Ranking Method (1985)

The first step in Chen's ranking method (1985) is to estimate the final composite $L(x)$ of alternative A_i. The final index value of the composite system is in the form of fuzzy numbers. With the help of index values, $L_{h=1}(x)$ and $L_{h=0}(x)$, the membership, $\mu(x)$ can be estimated.

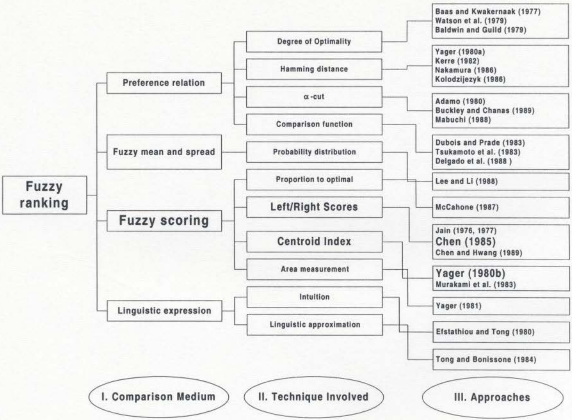


Figure 6.6. A taxonomy of fuzzy ranking methods (Chen and Hwang, 1992)

If there are "*m*" alternatives, there are *m* fuzzy numbers $[L(x),\ x = 1, 2, \ldots, m]$. The ranking of these "*m*" fuzzy numbers is done by maximising and minimising a set. The maximising set M is a fuzzy subset with membership function $\mu_M(L)$ given as

$$\mu_M(L) = \begin{bmatrix} \dfrac{(L - L_{min})}{(L_{max} - L_{min})}, & L_{min} \le L \le L_{max} \\ 0 & , \ OTHERWISE \end{bmatrix} \tag{6.3}$$

where, $L_{min} = min[minL_{h=0}(x)]$ and $L_{max} = max[maxL_{h=0}(x)]$ for $x = 1, \ldots, m$. Then the right utility value, $U_R(x)$, for alternative A_i is defined as

$$U_R(X) = max(min[\mu_M(L), \mu[L(x)]]) \tag{6.4}$$

The minimising set G is a fuzzy subset with membership function $\mu_G(L)$ given as

$$\mu_G(L) = \begin{bmatrix} \dfrac{(L - L_{max})}{(L_{min} - L_{max})}, & L_{min} \le L \le L_{MAX} \\ 0 & . \ OTHERWISE \end{bmatrix} \tag{6.5}$$

The left utility value, $U_L(x)$, for alternative A_i is defined as

$$U_L(X) = max(min[\mu_G(L), \mu[L(x)]]) \tag{6.6}$$

The total utility or ordering value for alternative A_i is

$$U_T(x)=\frac{U_R(x)+1-U_L(x)}{2} \tag{6.7}$$

The alternative, which has the highest ordering value, is selected as the best alternative. Chen (1985) has generalised the results for trapezoidal fuzzy numbers as shown in Figure 6.7.

$$U_T(x)=\frac{1}{2}\left[\frac{(d_i-L_{min})}{(L_{max}-L_{min})-(b_i-d_i)}+1-\frac{(L_{max}-c_i)}{(L_{max}-L_{min})+(a_i-c_i)}\right] \tag{6.8}$$

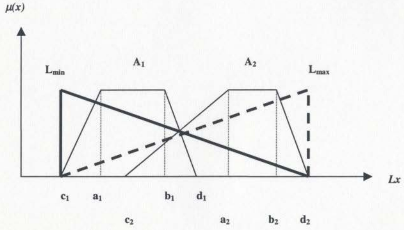


Figure 6.7. Chen (1985) ranking method for trapezoidal fuzzy numbers

Yager's Centroid Index Ranking Method (1980b)

In this category of ranking methodology, the centroid of the fuzzy number is determined. Each geometric centre corresponds to an *x* value on the horizontal axis. Yager (1980b) has proposed a ranking index as follows:

$$x_o = \frac{\int_0^1 g(x)\mu_i(x)\,dx}{\int_0^1 \mu_i(x)\,dx} \tag{6.9}$$

where *g(x)* is treated as a weight function measuring the importance of the value *x*. The denominator serves as a normalising factor whose value is equal to the area under the membership function μ_i. When $g(x) = x$ (linear weight), equation 6.9 gives the x_o (geometric centre). The value of x_o is the weighted mean value of fuzzy number *L(x)* and higher x_o values are considered better. Figure 6.8 shows a comparison of two fuzzy numbers and their centroids. The software Risk Calc (1995) estimates the centroid of a fuzzy number. The centroid is generally not the same as the mean except for scalars.

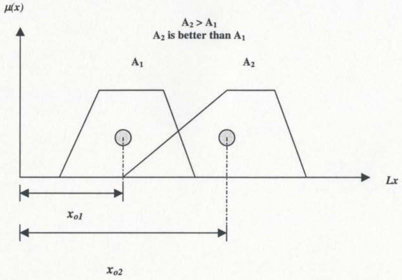


Figure 6.8. Yager's (1980b) centroid index method for ranking fuzzy numbers

Yager's estimate for ranking fuzzy numbers is not considered to be a very reliable method and Murakami et al. (1983) have modified this method. In this research, both Chen's (1985) and Yager's (1980b) methods were used to rank the alternatives.

6.2.5. WEIGHTING METHODS

MCDM methods require information about the relative importance of each attribute or criteria. The preference weights are estimated with the help of an importance matrix. They are normalised to sum to 1. In case of "*n*" criteria, a set of weights is

$$\underline{W}^T = (w_1, w_2, \ldots\ldots, w_j, \ldots\ldots, w_n) \qquad (6.10)$$

and

$$\sum_{j=1}^{n} w_j = 1 \qquad (6.11)$$

The MCDM problem becomes

$$D = \begin{array}{cc} & \begin{array}{cccccc} X_1 & X_2 & . & . & X_n \end{array} \\ \begin{array}{c} A_1 \\ A_2 \\ . \\ . \\ A_m \end{array} & \left(\begin{array}{cccccc} X_{11} & X_{12} & . & . & X_{1n} \\ X_{21} & X_{22} & . & . & X_{2n} \\ . & . & . & . & . \\ . & . & . & . & . \\ X_{m1} & X_{m2} & . & . & X_{mn} \end{array} \right) \end{array} \begin{array}{c} W \\ \left(\begin{array}{c} w_1 \\ w_2 \\ . \\ . \\ w_n \end{array} \right) \end{array} \qquad (6.12)$$

Hwang and Yoon (1981) described four different techniques for MCDM weighting schemes, which include: eigen-vector method, weighted least square method, entropy method and LINMAP. Saaty (1977) has introduced a method of scaling ratios using the principal eigen-vector of a positive comparison matrix. Weighting coefficients are assessed to reflect the relative importance of each attribute. Saaty (1988) suggested an analytical hierarchy procedure (AHP) to estimate the relative weight of each attribute in a group based on a paired comparison. To compare criterion "i" with "j" the decision-maker can assign value a_{ij} from Table 6.1.

Table 6.1. Linguistic measures of importance (Saaty, 1988)

Intensity of importance	Definition
1	Equal importance
3	Weak importance
5	Strong importance
7	Demonstrated importance
9	Absolute importance
2, 4, 6, 8	Intermediate values

He proposed the following steps to assign the weights:

a. If $a_{ij} = \tau$, then $a_{ji} = (1/\tau)$, where $\tau \neq 0$ and $i \neq j$;

b. If $i = j$, then $a_{ij} = a_{ji} = 1$; and

c. Construct matrix $A = (a_{ij} \mid i = 1,..., n; j = 1,..., n)$.

Saaty (1988) has shown that the eigen-vector corresponding to the maximum eigen value of matrix A is a cardinal ratio scale for the criteria compared. The eigen value problem can be solved by

$$A \cdot W = \Phi_{max} \cdot W \tag{6.13}$$

where, Φ_{max} is a scalar corresponding to the maximum eigen value and the unit vector "W" corresponding to Φ_{max} gives the preference weights.

Lu and Hu (1999) have suggested a simple technique for calculating the weights in water quality analysis. They used a decision matrix for three different factors: chlorophyll-a (C), phosphorous (P) and Secchi depth (S) for determining eutrophication effects. The relative importance of these factors can be assigned using values given in Table 6.1.

$$J = \begin{array}{cccc} \boldsymbol{P} & \boldsymbol{C} & \boldsymbol{S} & \\ 1 & 1/2 & 2 & \boldsymbol{P} \\ 2 & 1 & 3 & \boldsymbol{C} \\ 1/2 & 1/3 & 1 & \boldsymbol{S} \end{array} \tag{6.14}$$

A normalised matrix I is determined by normalising the matrix J column wise. The final weighted vector can be derived from summing the elements of each row of matrix I and normalising again for this vector.

$$I = \begin{bmatrix} 0.286 & 0.273 & 0.333 \\ 0.571 & 0.546 & 0.500 \\ 0.143 & 0.182 & 0.167 \end{bmatrix} \Rightarrow \begin{bmatrix} 0.892 \\ 1.617 \\ 0.4914 \end{bmatrix} \qquad (6.15)$$

Therefore after normalising to 1, the above equation becomes

$$\mathbf{W}^T = [\mathbf{P} \quad C \quad S] = [0.297 \quad 0.539 \quad 0.164] \qquad (6.16)$$

A double weighting scheme is proposed in composite programming (equation 6.2). The other type of weight used in CP is balancing factor (p_j). The balancing factor (p_j) is assigned to groups of indicators to reflect the importance of the maximum deviations, which represent maximum difference, an indicator value, and the best value for that indicator. The larger the value, the greater the concern with respect to the maximum deviation. When $p_j = 1$, all deviations are equally weighted, for $p_j = 2$, each deviation receives its importance in proportion to its magnitude (Torno et al., 1988).

6.2.6. CONVERTING STATISTICAL DATA INTO FUZZY NUMBERS

The concept of probability is usually related to the frequency of occurrence of events, obtained by repeated experiments. In contrast, fuzzy set theory could provide the appropriate framework to assess the possibility of events rather than their probability (Dubois and Prade, 1986). The most crucial step in the design of a problem that is to be solved by fuzzy set methods is the determination of membership functions (μ). There are many guidelines on developing membership functions for fuzzy sets. The fuzzy sets based on statistics are perhaps the most naturally fuzzy sets that can be used (Civanlar and Trussel, 1986).

The statistical data can be represented by histograms, which can be used for approximation of a probability density function (PDF). Consequently, the fuzzy sets using this histogram can follow the rule that, max $[\mu(x)] = 1$. A similar approach is used by Guyonnet et al. (2000) for comparing MC simulations and fuzzy sets as two methods of measuring uncertainties. Figure 6.9 shows that the highest frequency value (mode or MLV) is allotted a membership value of 1. Similarly the other values are also normalised proportionally.

Civanlar and Trussel (1986) have pointed out that from a heuristic point of view the elements that are most likely should have high membership values, however the set should be as selective as possible. These requirements are given below:

1. E $\{\mu(x) | x$ should be distributed according to underling probability density function (PDF);
2. $0 \leq \mu \leq 1$. Because an infinite scale is not necessary to assign grade of membership function; and
3. $\Sigma \mu^2$ should be minimised i.e. the fuzzy number should be as small as possibly.

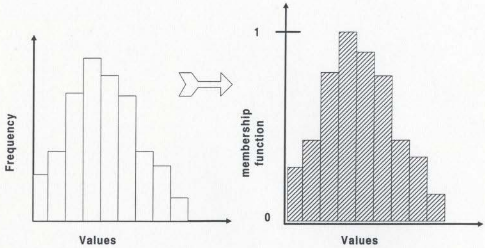


Figure 6.9 Conversion of statistical data into a fuzzy number

Jooste (2001) developed a simple methodology for risk estimation of co-occurring stressors in an aquatic ecosystem based on fuzzy sets. He used the lowest 5th, median and the highest 95th percentiles defining a triangular fuzzy number. A similar approach was adopted in this research. The confidence intervals of lowest 1% and highest 99% were used to define the largest likely interval of the fuzzy number. The mode or most frequent value was used to define the most likely value of the fuzzy number with a membership function value of 1. Figure 6.10 shows this methodology for developing a triangular fuzzy number from statistical data. The models developed in this research (Chapters 3-5) are statistical in nature. The values were converted into triangular fuzzy numbers using this technique.

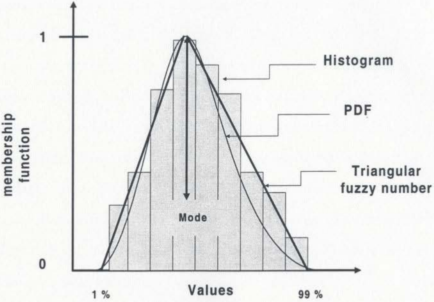


Figure 6.10. Methodology for developing a triangular fuzzy number

The next section focuses on the status of various types of treatment technology options available for offshore drilling operations. It helps in understanding the technical feasibility parameters of the treatment devices used for drilling waste risk management.

6.3. STATUS OF OFFSHORE TREATMENT TECHNOLOGY

The clean water act (CWA) requires the U.S. EPA to identify effluent reductions attainable through the application of a *Best Practicable Control Technology* (BPT). The U.S. EPA has estimated effluent levels based on the long-term average of the best existing treatment plants of various sizes and ages. The BPT is applied to conventional (BOD_5, *SS*, pH and fecal coliform etc.), toxic, and non-conventional pollutants. The CWA has recommended the *Best Conventional Pollutant Control Technology* (BCT) as an additional level of control for discharges of conventional pollutants from existing industrial point sources. The CWA has also established the *Best Available Technology Economically Achievable* (BAT) as their main feature to control the discharge of toxic and non-conventional pollutants. The BAT effluent limitation guidelines represent the best existing economically achievable performance of direct discharging plants. The important factors are the cost of achieving BAT effluent reductions, the age of equipment and facilities involved, processes used and engineering aspects of control technology, and non-water quality impacts etc. The BAT economic achievability is determined on the basis of the total cost to the industrial subcategory and the overall effect of the rule on the industry's financial health.

The U.S. EPA (2000b) supports pollution prevention technology (P2) by encouraging the appropriate use of SBFs. The U.S. EPA intends to control the discharge of SBFs, either by using state of the art technology and/or by encouraging the replacement of OBFs. The OBFs are subject to zero discharge requirements and land based disposals are recommended. The U.S. EPA has estimated drilling fluid retention values for solid control equipment used in the U.S. offshore (baseline solids control system) and for add on solids control systems (used in the North Sea), which are capable of reducing retention values lower than the baseline solids control system.

6.3.1. SOLID CONTROL SYSTEMS

The function of the solid control system is to separate drill cuttings from drilling fluid and at the same time maintain rheological properties of drilling fluids. The quality of drilling fluids deteriorates as the quantity of fine particles in the drilling fluid increases (Anon, 1999). The solid control system contributes to the fine particle fraction due to breakdown of larger particles. Therefore, the design and operation of the solid control system is important to limit the mechanical destruction of cuttings.

Separation of base drilling fluid is more difficult for WBFs than SBFs/OBFs. The solids have a tendency to disperse in the water phase. Therefore, different treatment techniques are used for WBFs and SBFs/OBFs. Additional treatments such as hydrocyclones and chemical flocculation units are used for WBFs. Typical solid control systems for SBFs drilling waste consist of primary and secondary shale shakers, a "drying" shale shaker or centrifuge which further removes the drilling fluid from the cuttings, a "high-G" shale shaker or centrifuge to remove fine solids, and a sand trap. Table 6.2 categorises various solid control devices. A brief description of various types of commonly used solid control devices is given in the following section.

Table 6.2. Drilling fluid recovery devices category

Unit Type	Category	G-Force
Linear motion shale shaker	Secondary shale shaker	6.25
Mud Cleaner	*FRU	
Decanting centrifuge	FRU	
Linear motion shale shaker	Dryer	8.0
Vibrating centrifuge	Dryer	130
Vertical centrifuge	Dryer	800
Squeezing press	Dryer	

*Fines removal unit

Shale Shakers

Shale shakers are vibrating screens used at primary and secondary levels of treatment. The primary or scalp shale shaker removes the larger size drill cuttings and protects downstream equipment from wear and tear. The primary shale shaker (PSS) recovers the drilling fluid from coarser size cuttings and sends the drilling fluid stream to a secondary shale shaker (SSS, mud cleaner). The cuttings from the primary shale shaker are sometimes sent to a new type of shale shaker, called a "drying" shaker or "cutting dryer", which treats cuttings, unlike the secondary shale shaker, which treats drilling fluid (Anon, 1999).

In shale shaker design, screen cloth characteristics, motion type, position and size of screen and arrangement of multiple screens are important parameters. The factor that differentiates primary and secondary shale shakers is the size of solids removed. The primary shale shakers have coarser screens than the secondary and the drying shale shakers. Longer retention times on shale shakers increase the degradation of solids on the screens. Flat screens provide the least retention time and surface area in comparison to other designs. Recently, corrugated screens are in vogue, which provide more surface area and more retention time, but at the same time more capacity as well. Downward slope orientation provides faster conveyance and less retention time compared to upward slope.

The U.S. EPA (2000b) has evaluated the operation of primary and secondary shale shakers for flat and corrugated screen deigns. Two tier shale shakers are very popular in the GOM (Gulf of Mexico). The U.S. EPA (2000b, 1999a) has observed that the downward sloping flat screens on the top tier minimise mechanical degradation of cuttings. The bottom tier is generally corrugated and slopes upward toward the discharge end. The cuttings from lower screens consist of smaller cuttings and mud type solids. These types of shale shakers require a force of 2 to 4G.

High-G Shale Shaker

The applied G force in this type of shale shakers ranges from 6 to 8G. The high-G shakers are used to remove fine particles from drilling fluid to maintain the viscosity of the drilling fluid stream. These shakers can also be used as "drying" shakers. The U.S. EPA (2000b, 1999a) has observed that high-G shale shakers are equipped with upward sloping corrugated screens. The solids discarded from high-G shale shakers are in the form of mud, but carry finer particles than the secondary shale shakers.

Centrifuges

Centrifuges are either a substitute for shale shakers or used as an add-on technology in addition to shale shakers. When centrifuges are used with shale shakers the efficiency of the solid control system increases by up to 30 or 40%. These units are installed in place of drying shale shakers. Recently, centrifuges have been used to recover SBFs from large cuttings; such centrifuges are very large in size and process all coarse and small drill cuttings.

Mud 10 is a combination of shale shaker and centrifuge. It has an internal rotating cone that vibrates and achieves very low retention of SBFs on cuttings (U.S. EPA, 2000b). A schematic of an arrangement of solid control system in the North Sea and GOM is shown in Figure 6.11. This solid control arrangement is able to reduce SBFs retention value to 3.85%. The centrifuge dryer is different from Mud 10 and has a vertically oriented screen centrifuge and has a very high-G value. The U.S. EPA (2000b) has reported that retention values are as low as 3.72% in that case.

Squeeze Press

Squeeze presses are used to separate attached drilling fluid from the bulk cuttings waste stream prior to discharge. The squeeze press creates a brick like solid chunk with entrapped drilling fluid. This is not widely used for recovering of drilling fluid. It can reduce the retention level to 6.71% SBFs on cuttings, which is in between the efficiency of primary shale shakers (9.32%) and centrifuges (3.7 to 3.85%). The efficiency of a squeeze press is also better than a secondary shale shaker (13.8%) and mud cleaner (11.9%).

Fines Removal Units (FRU) or Mud Cleaner

An acceptable level of fines (< 5 μm) is less than 5% in drilling muds. Higher levels lead to drilling problems due to changes in rheological properties of the drilling fluid. The U.S. EPA (2000b, 1999a) has suggested that where there are unfavourable formation characteristics, operators must be limited to diluting the fines in the active mud system through addition of fresh SBF and/or capturing a portion of fines in a container and sending the fines for disposal.

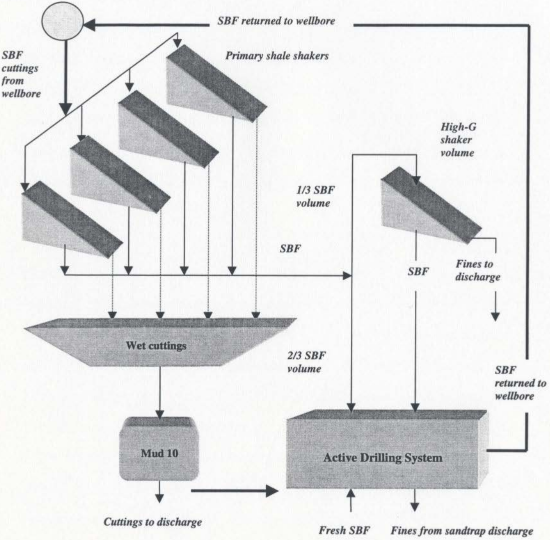


Figure 6.11. Configuration of Mud 10 solid control system (U.S. EPA, 2000b)

Thermal Treatment Units

The U.S. EPA (2000b) has investigated four thermal distillations and oxidation processes for removing oil from drill cuttings as a part of their final rulemaking. These technologies appeared to be promising in achieving their goal in oil based types of waste. But the U.S. EPA (2000b) has rejected them for further investigation because of associated difficulties with these technologies, which include installation offshore, operation of equipment, handling of processes waste and their by products, etc. The U.S. EPA (2000b) has also mentioned that using thermal distillation technologies offshore is getting popular for SBF waste treatment and recovery. The U.S. EPA (2000b) did not recommend these technologies for defining BAT limitations, although they are more popular in land based treatment processes.

6.3.2. PERFORMANCE OF SOLID CONTROL SYSTEMS

A primary shale shaker is generally a first treatment device in a solid control system. The secondary shale shaker receives drilling fluid/drill cuttings from primary shale shakers. The U.S. EPA (2000b) has estimated and reported long term average retention values of 10.6% by weight of synthetic base fluid on wet cuttings for a primary shale shaker and 15.0% for a secondary shale shaker. The U.S. EPA (2000b) has also provided retention data for a vibrating centrifuge, the add-on solid control technology that is currently in use in the North Sea. Based on available data, a long-term average of 5.14% by wet weight of synthetic base fluid can be achieved with a vibrating centrifuge.

The U.S. EPA (2000a, b) have proposed effluent limitation guidelines for the control of pollutant discharges associated with the retention on cuttings (ROC) of SBFs. The U.S. EPA used the statistics of performance of various solid control devices for the following reasons:

1. Estimating the quantities of current baseline pollutant discharges;
2. Calculating the potential effluent limits; and
3. Evaluating regulatory options.

The U.S. EPA (2000b) has selected two final numeric limits for the retention of SBFs on cuttings. For base fluid (e.g., ester) environmental properties - toxicity, biodegradation, and bioaccumulation - the average ROC should not exceed 9.4% by wet weight. A technology including horizontal and vertical centrifuges, squeeze presses, and high G dryers can be used. For other types of base fluids, the average ROC should not exceed 6.9% by wet weight. The U.S. EPA (2000b) has summarised percent retention of SBFs on cuttings based on three different technology types. These technologies include simple shale shaker systems (e.g., primary and secondary shale shakers etc.), cuttings dryers (e.g., horizontal centrifuge and Mud 10), vertical centrifuge, squeeze press, high G dryer and fines removal units (FRU) (e.g., decanting centrifuges and mud cleaners). The reported data are expressed by weight of SBF/weight of wet cuttings. The summary of data is given in Table 6.3.

Table 6.3. SBFs solid control system performance (modified after, U.S. EPA, 2000b)

Technology category/subcategory	No. of wells	Mean (μ)	Std. dev. (σ)	95th percentile
Primary shale shaker	32	9.32	3.05	14.3
Secondary shale shaker	22	13.8	3.48	19.5
Other shale shakers	22	8.96	1.78	11.9
Horizontal centrifuge (Mud 10)	26	3.85	2.01	7.16
Vertical centrifuge	8	3.72	1.54	6.26
Squeeze press	5	6.71	1.39	8.99
High-G dryer	6	9.40	2.17	13.0
Cuttings dryer I Horizontal centrifuge + Vertical centrifuge + Squeeze press + High-G dryer	45	4.89	2.72	9.37
Cuttings dryer II Horizontal centrifuge + Vertical centrifuge + Squeeze press	39	4.19	2.06	7.59
Cuttings dryer III Horizontal centrifuge + Vertical centrifuge + Squeeze press	34	3.82	1.89	6.93
Decanting centrifuge	22	9.97	2.27	13.7
Mud cleaner (FRU)	21	11.9	2.64	16.2
Fines removal Decanting centrifuge + Mud cleaner	39	10.8	2.51	14.9

The U.S. EPA (2000a, b) have compared the performance of different treatment technologies. For ester, the numeric limit is based on combining data from high-G dryer, squeeze press, horizontal centrifuge, and vertical centrifuge. The high-G dryer is important because it takes less space than other technologies. The U.S. EPA (2000b) has reported that in the development of a final numeric limit, 3 out of 6 high-G dryers, all 5 squeeze presses and 8 vertical centrifuges, and 25 horizontal centrifuges out of 26 complied with the numeric limit of 9.4%. The U.S. EPA (2000b) has also reported that all eight vertical centrifuges and 24 out of 26 horizontal centrifuges complied with a numeric limit of 6.9%.

The U.S. EPA (2000a, b) have suggested a baseline treatment train which includes primary shale shaker (PSS), secondary shale shaker (SSS), and fines removal units (FRU). The estimated volume contributions in a waste stream for the baseline control system are 78.5% (PSS), 18.5% (SSS) and 3% (FRU), respectively. Therefore, the synthetic base fluid percent attachment can be estimated as

$$\text{Baseline treatment} = (9.32 \times 0.785 + 13.8 \times 0.185 + 10.8 \times 0.03) = 10.20\ \%$$

The final cuttings waste stream retention values for BAT options 1 and 2 are given in Table 6.4. The U.S. EPA (2000b) has estimated the ROC values based on the cutting dryer I and the fine removal unit (FRU) given in Table 6.3.

Table 6.4. BAT weighted average compliance level solids retention

Options	Performance of system		Percent contributed (%)		Compliance level (% retention)
	Cuttings dryer	FRU	Cuttings dryer	FRU	
BAT I	3.82	10.8	97	3	4.03
BAT II			100	0	3.82

In the next section, the cost estimations are made for drilling fluid economic loss, treatment costs, human health and ecological damage costs etc.

6.4. COST ESTIMATION

In risk management, the optimisation of cost out of various feasible alternatives is one of the major objectives. Technically, various alternatives that can reduce the risk are possible to implement, but the decisive factor could be the cost to control that risk. The cost for various alternatives include the treatment cost, cost of loss of drilling fluid, economic loss due to lower production of commercially valuable ecological entities, human health damage cost, and possible non-water quality environmental damages. All cost estimates are reported in CAD $ in the following sections.

6.4.1. DRILLING FLUID COST

The U.S. EPA (2000b) has summarised the cost of SBFs, OBFs and WBFs drilling fluids. The U.S. EPA used $70.7/bbl for WBFs for their compliance cost estimates. The OBFs and SBFs per barrel cost estimates are $117.8 and $314, respectively. The OBFs cost data estimates are in the range of $109.9 to 141.3/bbl. The U.S. EPA (2000b) has suggested a mean value of $124/barrel for OBFs. The U.S. EPA (2000b) has estimated that within next few years the SBFs cost would be within range of $251.2 to 471/bbl. The U.S. EPA (2000b) has also suggested a mean value of $347/bbl for SBFs. Table 6.5 summarises the range and mean values for cost estimates of various drilling fluids on a per barrel basis.

The costs of drilling fluid loss are based on the amount attached to the cuttings, which can be determined for various discharge options.

Table 6.5. Drilling fluid per barrel cost ($) estimates

Drilling Fluid	Mean	Range
SBFs	347	251.2 - 471
OBFs	124	109.9 - 141.3
WBFs	70.7	

6.4.2. SOLIDS CONTROL TREATMENT COST

The U.S. EPA (2000b) has reported three best available technology options for control and treatment of SBF drill cuttings, which include:

1. Controlled discharge BAT option 1:

    (a) Limitations on stock synthetic base fluid (PAH content, biodegradation rate and sediment toxicity);

    (b) Limitations on discharged SBF-cuttings (no free oil, formation oil contamination, sediment and aqueous toxicity, retention on SBFs cuttings) discharged;

    (c) Limitations on Hg and Cd stock barite; and

    (d) Prohibition of diesel oil discharge

2. BAT discharge option 2: This is the same as the controlled discharge option except that retention of SBF on cuttings is based solely on the discharge from the cuttings dryer units, and does not include an allowance for the discharge of the fines removal units.

3. BAT option 3: Zero discharge option (Not considered in this research)

The U.S. EPA (2000a, b) have developed a methodology for calculating compliance cost for various options. They have summarised annual technology costs and pollutant loadings for drill cutting BAT options. The total treatment cost for year 1999 for various options is given in Table 6.6.

Table 6.6. Annual total technology cost for various BAT options in 1999

Options	Technology Cost ($/yr)
BAT option 1: Discharge with 4.03% retention of drilling fluid on cuttings	70,000,000
BAT option 2: Discharge with 3.82% retention of drilling fluid on cuttings	70,300,000
BAT option 3: Zero discharge	112,900,000

The U.S. EPA (2000a, b) have estimated per well waste volume using the number of drilling days required for different model wells from data provided by the American Petroleum Institute (API). Table 6.7 summarises the estimated drilling days for various model wells. Active drilling days comprise approximately 40% of the total time to drill, during which equipment is onsite. The actual days to drill can be calculated by multiplying by a factor of 2.5 to get active drilling days. For simplicity, one-month average time (30 days) was assumed to estimate the cost of solid control equipment rentals and for other expenditures.

Table 6.7. Drilling days for various model wells

Model well	Active drilling days	Actual drilling days
Shallow water development well	5.2	13.0
Shallow water exploratory well	10.9	27.3
Deep water development well	7.9	19.8
Deep water exploratory well	17.5	43.8

The U.S. EPA (2000b) has also reported the cost associated with onsite treatment of drill cuttings for the baseline and BAT options. For calculating the incremental compliance costs, the baseline solids control consisting of primary shale shaker followed by a secondary shale shaker is considered. The secondary shale shaker receives drilling fluid from the primary shale shaker and discharges smaller particle sized drill solids than the primary shaker (Anon, 1999). The purpose of the primary shale shaker is to receive the drilling fluid and drill cuttings coming from the bore hole and make the first separation of cuttings from the drilling fluid, whereas the secondary shale shaker is used to separate the smaller solid particles from the drilling fluid. The long-term average of 10.2% base fluid retained on wet cuttings is reported (U.S. EPA, 2000b).

Both BAT control options 1 and 2 can reduce the solids retention below the baseline retention value. The difference between two BAT options is not based on the use of different treatment technologies, rather it is identical for both options. In BAT option II, the FRUs are excluded. The technologies considered under the category of "cuttings dryers" includes vibrating centrifuges (horizontal and vertical), squeeze press units and high-G linear shakers. The cost of add-on technology is estimated as $ 3,768/day (US EPA, 2000b). The rental costs for various treatment devices are reported in Table 6.8.

Table 6.8. Cost estimates for various treatment units (U.S. EPA, 2000b)

Device type	Cost ($/day)
Shale shaker (Operation and Maintenance)	350 80
Mud 10 (vibrating horizontal centrifuge)	3768
Vertical centrifuge	1884
Mud cleaner (FRU)	300

The cost estimates for various treatment options are summarised in Table 6.9. The treatment costs are estimated based on daily rentals cost for a 30 day drilling period, installation and downtime cost, and monitoring analysis, which includes crude oil contamination testing, retention of base fluid testing (retort analysis) and sediment toxicity testing. The total costs of tests are normalised to one-month time to estimate the daily cost.

Four treatment options are considered to develop a relationship between % base fluid attached and treatment cost/day. These options include a baseline solid control system option, BAT options 1 and 2, and an extra option assumed in which the treatment units are primary and secondary shale shakers and a vertical centrifuge as a tertiary treatment device. In this option it is assumed that 60%, 20% and 20% waste is coming from primary, secondary and vertical centrifuges, respectively. The % base fluid attached is calculated by the following relationship:

Table 6.9. A single well cost estimates for various options
(modified after, U.S. EPA, 2000b)

Treatment option	Item	Cost ($)	Cost ($/day)
Baseline solid control system option (10.2%)	Treatment units		
	Shale shakers (2)		860
	FRU		300
	Installation and downtime cost	88,705	2,957
	Monitoring analysis		100
	Crude oil contamination test (@80/test)	80	
	Retention of base fluid (@80/test)	2,040	
	SedTox monitoring test	900	
	Total cost		**4217**
Extra option (9.1%)	Treatment units		
	Shale shakers (2)		860
	Vertical centrifuge		1,884
	Installation and downtime cost	88,705	2,957
	Monitoring analysis		100
	Crude oil contamination test (@80/test)	80	
	Retention of base fluid (@80/test)	2040	
	SedTox monitoring test	900	
	Total cost		**5,801**
BAT option I (4.03%)	Treatment units		
	Shale shaker		430
	FRU		300
	BAT solid control system	88,705	3,768
	Installation and downtime cost		2,957
	Monitoring analysis		100
	Crude oil contamination test (@80/test)	80	
	Retention of base fluid (@80/test)	2040	
	SedTox monitoring test	900	
	Total cost		**7,555**
BAT option II (3.82%)	Treatment units		
	Shale shaker		430
	BAT solid control system	88,705	3,768
	Installation and downtime cost		2,957
	Monitoring analysis		67
	Crude oil contamination test (@80/test)	80	
	Retention of base fluid (@80/test)	1020	
	SedTox monitoring test	900	
	Total cost		**7,222**

Extra option = $(9.32 \times 0.60 + 13.8 \times 0.20 + 3.72 \times 0.20) = 9.10\ \%$

The costs given in Table 6.9 do not include the cost of drilling fluid lost during ocean disposal in each treatment option. Based on synthetic base fluid % retention and daily estimated treatment cost data, a simple exponential relationship is fitted which is given below:

$$Cost\ (\$/day) = A \cdot e^{b \cdot (\%\ base\ fluid)} \tag{6.17}$$

Table 6.10 provides the details of the statistics of the above equation. The R^2 estimate is approximately 0.86, which shows a reasonably good fit. To find out the confidence interval (*CI*) at upper and lower bounds of the cost estimates, mean (μ) and standard deviation (or standard error, σ) can be used by performing Monte Carlo (MC) simulations. Figure 6.12 shows the fit of the regression equation.

Table 6.10. Regression statistics of treatment cost equation

Predictor	μ	σ	p	R^2	R^2_a
Ln (*A*)	9.20	0.158	0.000	85.6	78.5
Ln (*b*)	-0.074	0.022	0.075		

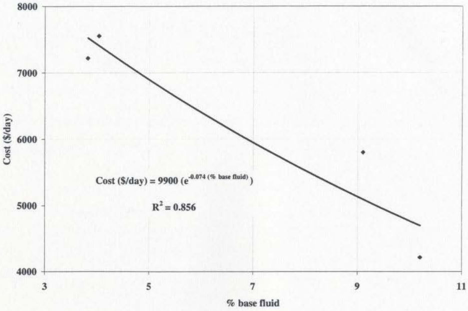


Figure 6.12. Fitted model for treatment cost and base fluid % retention

6.4.3. HUMAN HEALTH DAMAGE COST

Human health risk costs in a comparative risk project are costs associated with the incidence of environmentally induced illness in addition to regular illnesses in the absence of that particular environmental problem. Healthcare cost assessments in comparative risk projects have typically concentrated on medical costs and the cost of lost work time. Indirect costs stand for reduced productivity due to the lost work time and are estimated based on expected earnings during that lost time (U.S. EPA, 1993).

Table 6.11 summarises the daily health care costs associated with a variety of cancer and non-cancer illnesses. This cost includes direct and indirect costs. The values shown in

Table 6.11 are derived from the U.S. EPA (1993) and are projected to the year 2000 using a Consumer Price Index (CPI). According to the data given in Statistics Canada (2001) \$100 in 1986 is valued at \$139 in 1997 in the health and personal care sector. The discount rate is calculated as 3.05% by using compound interest formulae. The discount rate (*i*) is assumed constant over the time period and is used to project the cost estimates for the year 2000.

Table 6.11. Healthcare cost of cancer and non-cancer illnesses

Health Effect		Unit cost ($/d in 1990)	Unit cost ($/d in 2000)
Cancer	Non specific	279	377
	Respiratory	276	373
	Digestive	182	246
	Urinary	170	230
	Nervous system	599	809
	Leukaemia	328	443
	Others	196	265
Non-cancer	Asthma	0.21	0.28
	Digestive problems	11.1	15
	Headache*	0.033	0.052
	Non fatal heart attack*	258	405
	Hyper tension*	0.95	1.49
	Non fatal stroke*	189.3	297

*Values in 1985

$$F = P \cdot (1+i)^n \tag{6.18}$$

where

F = Future cost;

P = Present cost; and

n = Number of years

The human health costs are provided as daily treatment estimates. The population cancer risk estimates can be multiplied with any particular cancer cost value to calculate the cancer risk. The non-cancer risk is estimated in terms of HI and it does not provide any information regarding probability of illness (a major deficiency of the use of this measure for risk assessment!). For non-cancer risk cost estimation, HI_c can be related to qualitative estimates like low, medium and high as explained in section 6.2.1. These qualitative terms can be expressed by fuzzy numbers and can be added into other normalised cost estimates.

$$\textit{Non-cancer risk cost} = \textit{Qualitative estimates from Figure 6.5} \qquad (6.19)$$

6.4.4. ECOLOGICAL DAMAGE COST

Ecological damage due to disposal of toxic chemicals can affect commercial finfish and shellfish. The risk estimated to the whole ecosystem is assumed to be equal to the risk posed to the commercial fish. The ecological damage cost can be estimated by the following relationship:

$$\textit{Ecological damage cost (\$/day)} = \textit{Risk} \times \textit{Total fish (kg/day)} \times \textit{Cost of fish (\$/kg)} \quad (6.20)$$

where risk is the probability of adverse effects. Incorporating health care costs and ecological damage costs into economic damage assessment may be perceived to be double counting. The reasoning might be that if economic damage is due to prohibition in commercial fishing, people are not exposed to contaminated fish. However, it is important to recognize the distinction between physically enduring an illness and paying for health care. The rationale behind considering health care costs with ecological damage is that the economic burden is one that is borne in addition to the pain and suffering of illness (U.S. EPA, 1993). For any particular discharge scenario all these environmental costs are accumulated to make a trade off between cost and risk.

6.4.5. NON WATER QUALITY ENVIRONMENTAL DAMAGE COST

The elimination or reduction of water pollution may aggravate other environmental problems, which include air pollution (e.g., greenhouse gases, ozone depletion, acidification etc.), and solid waste disposal. The U.S. EPA (2000b) has evaluated the effects, which include air pollution, energy consumption, solid waste generation and management and affecting consumptive water use. The costs of these environmental effects are not included in this research.

6.5. RISK MANAGEMENT - A PROPOSED METHODOLOGY

In the previous and current chapters, a step by step methodology is developed for estimating the fate of drilling waste discharges in the marine environment and its related ecological and human health risks. The estimated risks can be linked to various treatment technology options as well as economical damages and treatment costs. A framework for applying the various models is illustrated in Figure 6.15. This framework can be followed to make a risk-cost tradeoff analysis for various available alternatives.

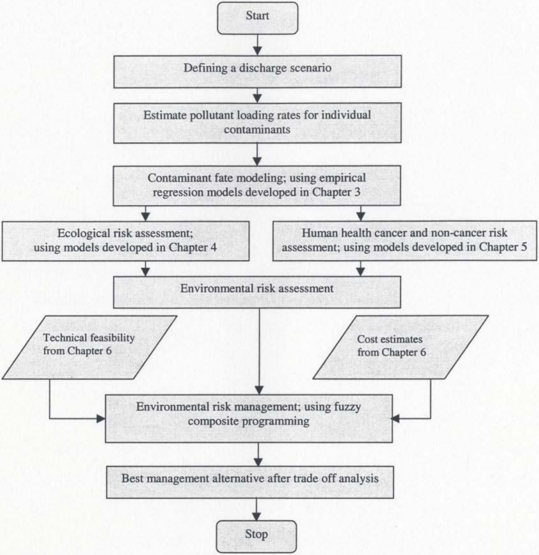


Figure 6.15. Proposed research framework for risk management of drilling waste discharges

Various discharge scenarios based on synthetic base fluid attached to the drill cuttings can be defined to determine the pollutant loading rates for contaminants present in drilling waste. The contaminant fate models were used to estimate the predicted environmental concentrations of pollutants in water column and sediment pore water. The ecological and human health risk assessments were performed based on the exposure concentration. The ecological and human health risks were combined to determine the total environmental risk posed by the drilling waste discharges. The risk management methodology using fuzzy composite programming was used to determine the best drilling waste discharge scenario.

The research framework shown in Figure 6.15 is applied to a hypothetical case study on the East Coast of Canada in the next chapter. Various discharge scenarios based on base fluid percent attached to the drill cuttings were selected to investigate the best discharge option from minimum environmental risk, maximum cost saving and technical feasibility points of view.

Chapter 7

RISK MANAGEMENT OF DRILLING WASTE DISCHARGES IN THE MARINE ENVIRONMENT - A HYPOTHETICAL CASE STUDY

This chapter deals with a hypothetical case study of an oilfield on the East Coast of Canada. The models developed in the previous chapters are integrated to show the significance of adopting a holistic risk management methodology for the selection of the best management alternative or a discharge scenario for drilling waste disposal in the marine environment.

A risk-based methodology framework developed was used for a hypothetical case study in this chapter. Firstly, some basic information about the oilfield developments in the Grand Banks is presented. Various discharge scenarios representing management alternatives are selected based on regulatory discharge requirements and efficiency of the state-of-the-art solid control devices. Based on these selected discharge scenarios, the loading rates for contaminants present in the drilling waste stream are estimated. The fate models developed in Chapter 3 were employed in estimating the *PEC* in the water column and pore water. In the next step, the ecological and human health risk assessment models were used for risk characterization, which are based on estimated exposure concentrations (*EC*). In the end, a tradeoff analysis was performed to decide the best management alternative for the discharge of drilling waste from risk reduction, cost saving and technical feasibility viewpoints.

7.1. INTRODUCTION

The Grand Banks is one of the biggest offshore oil exploration and development sites in Canada. These fields contain huge quantities of natural gas reserves. More than 115 wells have been drilled in the Grand Banks up to year 2000 and they include crude oil reserves of more than 2-billion bbl capacity. The Canada-Newfoundland Offshore Petroleum Board (CNOPB) has estimated reserves of 2.1 billion bbl of crude oil, 1.640 billion bbl of natural gas, and 413 million bbl of natural gas liquid (NGL) on the Grand Banks (CNOPB, 2001).

The Grand Banks are situated to the southeast of Newfoundland covering 93,200 km^2. The Grand Banks are the part of the North American continental shelf in the Atlantic Ocean (see Figure 7.1). It is an international fishing ground, which extends 560 km north-to-south and 675 km east-to-west. The Grand Banks average water depth is 55 m, but at many places reaches to 180 m. The cold Labrador Current and the relatively warm Gulf Stream meet in the vicinity of the Grand Banks which often causes heavy fog. The mixing of the cold and warm waters produces favorable conditions for the growth of plankton, which is an essential element in the foodweb of commercial fish (CNOPB, 2001).

Hibernia was the first oilfield on the Grand Banks. It started production with a capacity of approximately 175,000 bbl/day in 1997. The Hibernia oilfield has estimated reserves of

884 million bbl crude oil, 247 billion bbl of natural gas and 145 million bbl of NGL. A gravity-based production system (GBS) is used at the Hibernia oilfield (CNOPB, 2001). The second important offshore oil project on the Grand Banks is Terra Nova. The Terra Nova oilfield has an estimated 406 million bbl of oil reserves. It will start oil production in 2002. The Terra Nova development project is using a floating production and offloading system (FPSO).

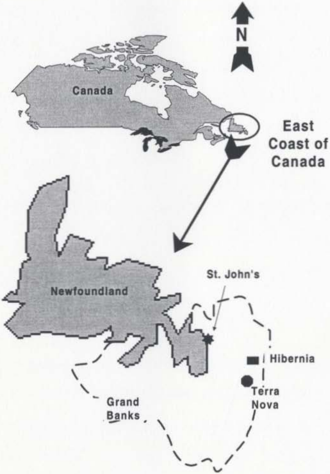


Figure 7.1. Grand Banks and the oilfields on the East Coast of Canada
(not drawn to scale)

A new development on the Grand Banks is the White Rose field, which has estimated reserves of 250 million bbl. This project is in the beginning of the permitting process for development, with a production start-up target in year 2004. Other structures in the basin include Hebron-Ben Nevis and Riverhead, which are under exploration or appraisal as potential projects for future developments (CNOPB, 2001).

Other than oil exploration/production, the extensive use of the area by trawler fleets has led to overfishing which caused depletion in fish production. The Grand Banks fish resource includes cod, haddock, rosefish, various types of flatfish, herring, and mackerel etc. In 1977, Canada extended its fishing areas within 370 km of its shores, which includes most of the Grand Banks (Britannica, 2001).

7.2. A HYPOTHETICAL OILFIELD ON THE EAST COAST OF CANADA

A hypothetical oilfield is considered on the Grand Banks of Newfoundland. It is approximately 35 km southeast of the Hibernia project and covers an area of 67 km^2. The field is located in water approximately 95 m deep.

Drilling of approximately 32 wells is associated with this oilfield, which results in substantial discharges of drilling wastes. Drilling wastes consist primarily of the spent muds, rock and a variety of additives, which are generated during drilling. The elements of greatest concern in these wastes are base fluid, heavy metals and formation oil, although the cuttings themselves are also a concern because of their smothering effect on the benthic community.

The environmental impact statement indicates that drilling wastes will be discharged over approximately 67 km^2 of the Project area. Even after the treatment of drilling wastes, over 1,400 m^3 of base oil will be released into the marine environment during the life of the project. The operators are committed to a minimum-release policy by using state-of-the-art technology to control potentially harmful discharges. They have proposed the use of technology that reduces the oil discharged in dry cuttings to a 7 - 8% ROC as against the currently regulated 15% on the East Coast.

Major finfish and invertebrates stocks have changed drastically in the last 15 years in Newfoundland waters. Traditionally cod used to dominate catches, but in the last few years cod stocks have declined and other commercial species became important. By 1994 the catch statistics pertaining to these species have changed appreciably. The five most important species in the hypothetical study area, based on total landings at Newfoundland ports are: *stimpson surf clam, snow crab, Iceland scallops, skate and redfish*. The Terra Nova environmental impact assessment report (1996) has also summarized the names of various commercial species found in different parts of the Grand Banks. The Newfoundland port landings of these species from the study area were *capelin, squid, herring* and *mackerel*. The total quantity of commercial landings to Newfoundland ports was estimated to be 2110 tons (Table 7.1).

7.3. CONTAMINANT FATE MODELING

The risk-based decision methodology developed in this research was applied to the hypothetical case study of this oilfield. Some necessary assumptions and simplifications were made to fill in the missing information and streamline the complexity of a real world problem. Based on the available information, following necessary assumptions were made:

Table 7.1. Total landings of each species in Newfoundland (Terra Nova, 1996)

Species (Grand Bank)	Quantity (tons)	Species (Study area)	Quantity (tons)
Clam	11,092	*Squid*	95
Redfish	1,495	*Herring*	973
Skate	1,940	*Mackerel*	5
Snow crab	4,742	*Capelin*	1,037
Iceland scallop	4,033	Total commercial fish landed at Newfoundland ports	2,110
All other species	1,100		
Total	24,402		

1. The hypothetical oilfield consists of approximately 32 wells, which encompass an affected area of 67 km^2. The wells were assumed to be uniformly distributed over that area. The affected impact area (A_w) for a single well was 2.09 km^2. The radius of impact area (R) for a single well was approximately 816 m. The depth of water column was 95 m.

2. The disposed drilling waste was assumed to be completely mixed in the impact area under steady state conditions.

3. The wells were assumed to be drilled only by SBFs. The esters are the most commonly used and environmentally benign synthetic based drilling fluids (U.S. EPA. 2000a). The physico-chemical characteristics of esters are more extensively reported in the literature than the other synthetic drilling fluids. and these were used in this case study (Chapters 2 and 3).

4. Pollutant loading rates of heavy metals. base fluid (ester) and organic priority pollutants were calculated based on deep development model well data as suggested by U.S. EPA (2000a. b).

5. For human health risk assessment. it was assumed that only St. John's and its suburban population (165.000) are exposed to all contaminated fish that is caught from the affected area.

7.3.1. ESTIMATION OF POLLUTANT LOADING RATES

To determine the pollutant concentration in the water column and pore water. the total pollutant loading rates for each discharge option were estimated. For this purpose. the U.S. EPA (2000a. b) assumed that the suspended solids (*SS*) concentration is attributed to drill cuttings in the waste stream. The density of dry cuttings is reported to be 2.57 kg/L in the literature (U.S. EPA. 2000a). The total volume of dry cuttings for a development well is approximately 140 m^3 (U.S. EPA. 1999a). This volume includes borehole volume and an additional 7.5% wash out from the walls of the wells.

Five discharge scenarios were selected as potential management alternatives for drilling waste disposal in a marine environment. These alternatives include 10% (current practice in Gulf of Mexico), 8.5% (obtainable with the current technology), 7.0%, 5.5% and 4.0% (BAT proposed). These alternatives represent the percentage of base fluid attached to the wet cuttings. Table 7.2 provides a detailed step-by-step approach for estimating the amounts of *SS* and base fluid expected to be released into the environment for the 10% discharge option.

The SBF consists of 47% base fluid (ester), 33% barite and 20% water. The density of drilling waste depends on the amount of base fluid attached to the drill cuttings. The major components of drilling wastes are dry drill cuttings, base fluid, barite and water. The weights and volumes of these components were calculated based on ester percentage attached to the cuttings. The volume and weight of dry drill cuttings were estimated using borehole volume and density of dry cuttings.

The quantities of each component were estimated to determine the weight and volume of total drilling waste for a given discharge option. The total volume of base fluid discharged for the 10% discharge option was estimated to be 57 m^3. The amount of formation oil was estimated based on an assumption that it is 0.2% volume fraction of the SBF, which is 140 kg for the 10% discharge option. The weight of barite disposed under the 10% discharge option is approximately 32,000 kg. The barite discharged in the marine environment contributes trace heavy metals, which pose a threat to ecological entities.

Table 7.2. A methodology for estimating of drilling waste different constituents (10% attached base fluid).

Items	Water	Base fluid	Barite	DC	Form. oil
% SBF	20	47	33	N/A	N/A
Density (kg/m^3)	1000	792	4240	2575	832
DC (includes 7.5% washout, m^3) = Length · (Area of cross section) · 1.075				137.2	
DC (kg) = 137.2 (m^3) · 2575 (kg/m^3)				353,150	

Items	Formulation	Scenario 1
Base fluid attached	After treatment the % on wet cuttings	10.0%
SBF fraction to the TW	(Fraction base fluid attached) · TW/0.47	0.213
TW (kg)	DC/(1 - SBF fraction to the TW)	452,935
Water (kg)	0.2 · (SBF fraction to the TW) · TW	19,100
Water (m^3)	Water (kg)/1000	19.1
Barite (kg)	0.33 · (SBF fraction to the TW) · TW	31,835
Barite (m^3)	Barite (kg)/4240	7.51
Base fluid (kg)	(Base fluid attached) · TW	45,294
Base fluid (m^3)	Base fluid (kg)/792	57.2
SBF (m^3)	Σ (Water, Barite, Base fluid) $_{(m^3)}$	84.0
SBF (kg)	Σ (Water, Barite, Base fluid) $_{(kg)}$	96,230
SBF (kg/m^3)	SBF (kg)/SBF (m^3)	1,146
Form. oil (m^3)	0.002 · SBF (m^3)	0.168
Form. oil (kg)	Form. oil (m^3) · 832	140
Total oil (m^3)	Σ (Form. oil, Base fluid) $_{(m^3)}$	57.4
Total oil (kg)	Σ (Form. oil, Base fluid) $_{(kg)}$	45,433
Total drilling waste (m^3)	Σ (DC, Water, Barite, Base fluid, Form. oil) $_{(m^3)}$	221.3
Total drilling waste (kg)	Σ (DC, Water, Barite, Base fluid, Form. oil) $_{(kg)}$	453,075
Drilling waste density (kg/m^3)	Total drilling waste (kg)/Total drilling waste (m^3)	2047
Volume fraction of SBF	SBF (m^3)/Total drilling waste (m^3)	0.380
Weight fraction of barite	Barite (kg)/Total drilling waste (kg)	0.0703
Total suspended solids (kg)	Σ (Barite, DC) $_{(kg)}$	384,830

TW: Total weight DC: Dry cuttings

The density of drilling waste for the 10% discharge option was estimated to be 2.05 kg/L. The volume fraction of SBF and the weight fraction of barite in the total drilling waste were calculated for estimating pollutant loading rates (*E*). A similar procedure was repeated for other discharge options. The weights and volumes estimated for different components of drilling waste are summarized in Table 7.3.

The drilling waste density increases with a decrease in the percentage base fluid attached to the drill cuttings. The drilling waste densities estimated are 2.05, 2.12, 2.17, 2.25, and 2.33 kg/L for the 10%, 8.5%, 7%, 5.5% and 4% discharge options, respectively. The volumes of base fluid discharged with cuttings vary from 57 to 20 m^3 for the 10% to 4% discharge options, respectively. The amounts of barite discharged ranged from 32,000 to 11,000 kg, approximately. The total weight of drilling waste varies from 453,000 to 386,000 kg for 10% to 4% discharge options, respectively. There is not an appreciable difference in total quantity of drilling waste because the total weight of dry cuttings is the same for all discharge options.

The amounts of heavy metals depend on the quantity of barite discharged for each option. The effluent concentrations of heavy metals in drilling waste were estimated based on the weight fractions of metals in the barite, whereas organic pollutant concentrations depend on the volume fraction of formation oil present in the SBF. The volume fraction of SBF was calculated by dividing the volume of SBF with the total volume of drilling waste for a given discharge option. The estimated volume fractions of SBFs are 0.378, 0.331, 0.282, 0.229 and 0.173 for the 10%, 8.5%, 7%, 5.5% and 4.0% discharge options, respectively. Similarly, the barite weight fractions were estimated by dividing the weight of the barite by the total weight of drilling waste for a given discharge option. The estimated barite weight fractions are 0.0702, 0.0597, 0.0491, 0.0360 and 0.0281 for the 10%, 8.5%, 7%, 5.5% and 4.0% discharge options, respectively.

The SBF volume and barite weight fractions in the drilling waste stream were used in estimating the organic pollutant and heavy metals concentrations (C_E) in the drilling waste, respectively. Table 7.4 describes the mass balance equations used for estimating the C_E. A summary of SBF volume fraction and barite weight fractions in drilling waste for different discharge options is given in Table 7.4.

The typical amounts of trace heavy metals (As, Cd, Cu, Cr, Hg, Pb, Ni and Zn) in mg per kg of barite are reported in Chapter 2 (U.S. EPA, 1999a). These values were used to estimate the concentrations of different heavy metals in drilling waste. Similarly, the naphthalene concentration in formation oil is required to estimate its effluent concentration (C_E) in drilling waste. The effluent concentrations for different discharge options were estimated based on the formulation given in Table 7.4. The heavy metals in mg/kg of barite and naphthalene in mg/ml of formation oil were used in this formulation (Table 2.5). The pollutant effluent concentrations in the drilling waste stream were estimated for various discharge options (Table 7.5). The ester (base fluid) concentration in the drilling waste was determined by dividing the total weight of ester discharged with the total volume of drilling waste estimated for that discharge option (see Table 7.3).

Table 7.3. Estimation of drilling waste constituents for different discharge scenarios.

Base fluid attached with cuttings (% of TW)		10.0	8.5	7.0	5.5	4.0
SBFs fraction in total weight (TW)		0.213	0.181	0.149	0.117	0.085
Dry cuttings (DC) (including 7.5% washout)	Weight (kg)	353,150	353,150	353,150	353,150	353,150
	Volume (m^3)	137.2	137.2	137.2	137.2	137.2
	Density (kg/m^3)	2,575	2,575	2,575	2,575	2,575
Total weight (TW)	Weight (kg)	452,935	430,956	414,795	399,803	385,856
	Volume (m^3)	221.1	205.2	179.5	178.0	165.8
	Density (kg/m^3)	2,048	2,100	2,310	2,246	2,327
Ester	Weight (kg)	45,294	36,631	29,036	21,989	15,434
	Volume (m^3)	57.2	46.2	36.7	27.8	19.5
	Density (kg/m^3)	792	792	792	792	792
Barite	Weight (kg)	31,835	25,720	20,387	15,439	10,837
	Volume (m^3)	7.51	6.06	4.81	3.64	2.55
	Density (kg/m^3)	4,240	4,240	4,240	4,240	4,240
Water	Weight (kg)	19,100	15,588	12,356	9,357	6,568
	Volume (m^3)	19.1	15.8	12.5	9.4	6.6
	Density (kg/m^3)	1000	1000	1000	1000	1000
Form. Oil (0.2%)	Weight (kg)	139.7	113.2	89.7	68.0	47.7
	Volume (m^3)	0.17	0.14	0.11	0.08	0.06
	Density (kg/m^3)	832	832	832	832	832
SBFs (Ester + barite + water)	Weight (kg)	96,230	77,939	61,778	46,785	32,839
	Volume (m^3)	84.0	68.1	53.9	40.9	28.7
	Density (kg/m^3)	1,146	1,146	1,146	1,146	1,146
Total oil (Ester + form. oil)	Weight (kg)	45,433	36,745	29,125	22,057	15,482
	Volume (m^3)	57.4	46.4	36.8	27.8	19.6
	Density (kg/m^3)	792	792	792	792	792
Total drilling waste (including form. oil)	Weight (kg)	453,075	431,069	414,885	399,871	385,904
	Volume (m^3)	221.4	205.3	191.2	178.0	165.9
	Density (kg/m^3)	2,047	2,100	2,170	2,246	2,327
	Density (kg/L)	2.05	2.10	2.17	2.25	2.33

Table 7.4. Estimation of pollutants effluent concentrations in drilling waste stream.

Organic pollutants:
Vol. fraction of form. oil = Vol. of form. oil/Vol. of SBFs = 0.002; and
Vol. fraction of SBFs = Vol. of SBFs/Vol. of total drilling waste.

C_E, Effluent conc. (mg/L) = (mg of pollutant/ml of form. oil) · (Vol. fraction of form. oil)·
(Vol. fraction of SBFs) · (1000 ml/L)

Heavy metals:
Wt. fraction of barite = (Wt. of barite/Total drilling waste)
C_E, Effluent conc. (mg/L) = (mg/kg of barite) · (Wt. fraction of barite) · (Drilling waste density, kg/L)

Attached base fluid (%)	10.0	8.5	7.0	5.5	4.0
Vol. fraction of SBFs	0.378	0.331	0.282	0.229	0.173
Wt. fraction of barite	0.0702	0.0597	0.0491	0.0386	0.0281
Density of drilling waste (kg/L)	2.05	2.10	2.17	2.25	2.33

7.3.2. PREDICTED ENVIRONMENTAL CONCENTRATION (*PEC*)

The effluent concentrations (C_E) of pollutants in drilling waste were now used for estimating the loading rate (*E*) for each discharge scenario. The regression models developed in Chapter 3 were used to determine the predicted environmental concentrations (*PEC*) in the water column and sediment pore water. The *PEC* represents the highest 95th percentile of water column and pore water concentration cumulative distributions.

First, the total quantities of pollutants were estimated by multiplying the total volume of the drilling waste with the C_E of each pollutant present in the drilling waste stream for a given option. The actual time of drilling may vary from 13 to 44 days for different types of wells (U.S. EPA, 2000a). An average time of one-month is assumed to estimate the loading rates for each pollutant. The loading rates for all pollutants are provided in mg/hr, except for ester, which is given in kg/hr. Table 7.6 provides a summary of pollutant loading rates estimated for different discharge scenarios.

Table 7.5. Concentrations of pollutants in drilling waste for different discharge scenarios.

Pollutants	*BF*	C_E, Concentration of pollutants in drilling waste (mg/L) before disposal for various discharge scenarios				
		10.0%	8.5%	7.0%	5.5%	4.0%
As	1.000	1.0133	0.8893	0.7571	0.6156	0.4639
Cd	0.994	0.1570	0.1378	0.1173	0.0954	0.0719
Cr	0.993	34.2510	30.0620	25.5908	20.8079	15.6796
Cu	0.830	2.6687	2.3423	1.9940	1.6213	1.2217
Hg	0.850	0.0143	0.0125	0.0107	0.0087	0.0065
Ni	0.990	1.9266	1.6910	1.4395	1.1704	0.8820
Pb	0.951	5.0092	4.3966	3.7427	3.0432	2.2931
Zn	0.946	28.6139	25.1143	21.3790	17.3833	13.0990
Naphthalene	1.000	1.0800	0.9479	0.8069	0.6561	0.4944
*Ester	1.000	0.2027	0.1785	0.1519	0.1236	0.0931

*Values are in kg/L

The impact radius (*R*) of 816 m was used to estimate the *PEC* from regression models developed in Chapter 3. These regression models were used to estimate the *PEC* in the water column and pore water. Table 7.7 provides a summary of mean *PEC* values (of 95th percentile) in the water column. The background mean sea level concentrations are also provided for a comparison.

Table 7.6. Pollutant loading rates, *E* (mg/hr) for different discharge scenarios.

Pollutants	10%	8.5%	7.0%	5.5%	4.0%
As	310.5	253.6	201.0	152.3	106.9
Cd	48.1	39.3	31.2	23.6	16.6
Cr	10495.1	8573.3	6795.6	5146.4	3612.3
Cu	817.7	668.0	529.5	401.0	281.5
Hg	4.4	3.6	2.8	2.1	1.5
Ni	590.4	482.3	382.3	289.5	203.2
Pb	1534.9	1253.8	993.9	752.7	528.3
Zn	8767.8	7162.3	5677.1	4299.4	3017.8
Naphthalene	330.9	270.3	214.3	162.3	113.9
*Ester	62.3	50.9	40.3	30.5	21.4

*Ester (values are in kg/hr)

The estimated concentrations of pollutants in the water column are too low to cause any damage to the ecological community. The concentration of ester in the water column varies from 2.56×10^{-3} to 8.79×10^{-4} µg/L for the 10% to 4% discharge options, respectively. Similarly, for other pollutants, the *PECs* are lower than the corresponding background concentrations with a difference of orders of magnitudes. By comparing water column *PEC* with background level concentrations it can be concluded that water column exposure is not a real threat to the ecological entities. This conclusion is in harmony with the U.S. EPA findings (2000a, b).

Table 7.7. Mean values of *PEC* (µg/L) in the water column for different discharge scenarios.

Pollutants	Mean sea concentration	10%	8.5%	7.0%	5.5%	4.0%
As	3.70E-2	1.62E-07	1.32E-07	1.04E-07	7.91E-08	5.54E-08
Cd	4.40E-2	1.68E-08	1.37E-08	1.08E-08	8.20E-09	5.75E-09
Cr	7.90E-2	6.13E-07	5.00E-07	3.96E-07	3.00E-07	2.10E-07
Cu	7.20E-1	1.10E-07	8.94E-08	7.08E-08	5.36E-08	3.76E-08
Hg	5.40E-2	1.23E-12	1.01E-12	7.98E-13	6.03E-13	4.25E-13
Ni	4.00E-1	2.15E-07	1.76E-07	1.40E-07	1.06E-07	7.43E-08
Pb	4.80E-1	2.40E-07	1.96E-07	1.55E-07	1.17E-07	8.24E-08
Zn		6.51E-07	5.32E-07	4.22E-07	3.19E-07	2.24E-07
Naphthalene	7.00E-1	1.02E-14	8.31E-15	6.60E-15	5.00E-15	3.52E-15
Ester		2.56E-03	2.09E-03	1.65E-03	1.25E-03	8.79E-04

The other exposure to marine organisms is the pore water concentration. The higher density of drilling waste and the affinity of pollutants to attach themselves to sediments are the major causes of higher concentrations in pore water. The mean values of *PEC* in pore water for ester are 24.6, 20.1, 16.0, 12.1 and 8.5 mg/L for the 10%, 8.5%, 7%, 5.5% and 4.0% discharge options, respectively (Table 7.8). The pore water *PECs* for naphthalene and Hg are the only two pollutants whose concentrations are below background level concentrations. For all other pollutants considered, the pore water *PEC* values are higher than background concentrations. The mean *PEC* values for As vary from 0.32 to 0.11 mg/L for 10% to 4% discharge option. For Cd, the mean *PEC* varies from 0.23 to 0.08 mg/L for the 10% to 4% discharge options. The mean *PEC* values for other pollutants are summarized in Table 7.8.

Table 7.8: Means and standard deviations of pore water *PEC* (μg/L) for different pollutants in discharge scenarios.

Pollutants	Mean sea concentration	10%	8.5%	7.0%	5.5%	4.0%
As	3.70E-2	3.20E+02 (2.03E+00)	2.61E+02 (1.64E+00)	2.07E+02 (1.25E+00)	1.57E+02 (9.49E-01)	1.10E+02 (6.53E-01)
Cd	4.40E-2	2.32E+02 (4.58E+00)	1.90E+02 (3.81E+00)	1.50E+02 (2.99E+00)	1.14E+02 (2.20E+00)	8.00E+01 (1.49E+00)
Cr	7.90E-2	2.87E+03 (4.03E+01)	2.35E+03 (3.26E+01)	1.86E+03 (2.58E+01)	1.41E+03 (1.88E+01)	9.89E+02 (1.33E+01)
Cu	7.20E-1	1.70E+03 (3.39E+01)	1.39E+03 (2.71E+01)	1.10E+03 (2.09E+01)	8.32E+02 (1.55E+01)	5.84E+02 (1.02E+01)
Hg	5.40E-2	5.28E-05 (2.51E-07)	4.32E-05 (2.04E-07)	3.42E-05 (1.62E-07)	2.59E-05 (1.19E-07)	1.83E-05 (8.52E-08)
Ni	4.00E-1	2.83E+03 (7.00E+01)	2.32E+03 (5.49E+01)	1.84E+03 (4.36E+01)	1.39E+03 (3.22E+01)	9.77E+02 (2.24E+01)
Pb	4.80E-1	3.20E+03 (5.76E+01)	2.61E+03 (4.51E+01)	2.07E+03 (3.43E+01)	1.57E+03 (2.58E+01)	1.10E+03 (1.75E+01)
Zn		3.46E+03 (4.74E+01)	2.82E+03 (3.85E+01)	2.24E+03 (3.05E+01)	1.70E+03 (2.23E+01)	1.19E+03 (1.58E+01)
Naphthalene	7.00E-1	5.16E-07 (2.74E-09)	4.21E-07 (2.16E-09)	3.34E-07 (1.70E-09)	2.53E-07 (1.26E-09)	1.78E-07 (8.18E-10)
Ester		2.46E+04 (4.19E+01)	2.01E+04 (3.39E+01)	1.60E+04 (2.41E+01)	1.21E+04 (1.89E+01)	8.48E+03 (1.21E+01)

* The values in parenthesis show standard deviation

The standard deviations of *PEC* estimates for pore water are also reported in Table 7.8 for all contaminants. The values are reported in parenthesis. These values account for uncertainty in the pore water *PEC* estimates. The uncertainties in the coefficients of the

The estimated *PEC* values (Table 7.8) were multiplied with *p* and the corresponding *BF* to determine the actual exposure concentrations (*EC*). Table 7.9 summarizes the mean *EC* of pollutants for various discharge scenarios. The exposure concentrations calculated were used for ecological and human health risk assessments in the subsequent analyses.

Table 7.9. Mean exposure concentration in pore water (μg/L) for different discharge scenarios.

Pollutants	10%	8.5%	7.0%	5.5%	4.0%
As	0.23	0.19	0.15	0.11	0.08
Cd	0.17	0.14	0.11	0.08	0.06
Cr	2.05	1.68	1.33	1.01	0.71
Cu	1.01	0.83	0.66	0.50	0.35
Hg	0.00	0.00	0.00	0.00	0.00
Ni	2.01	1.65	1.31	0.99	0.70
Pb	2.19	1.78	1.42	1.07	0.75
Zn	2.35	1.92	1.52	1.16	0.81
Naphthalene	0.00	0.00	0.00	0.00	0.00
Ester	17.68	14.45	11.50	8.70	6.10

7.4. ECOLOGICAL RISK ASSESSMENT

The risk characterization of ecological entities is based on dose response relationships. The estimated dose or exposure is compared with the response for each contaminant, which were established in Chapter 4. The following specific steps were performed in the ecological risk assessment:

The estimated *PEC* values (Table 7.8) were multiplied with *p* and the corresponding *BF* to determine the actual exposure concentrations (*EC*). Table 7.9 summarizes the mean *EC* of pollutants for various discharge scenarios. The exposure concentrations calculated were used for ecological and human health risk assessments in the subsequent analyses.

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Cd	0.17	0.14	0.11	0.08	0.06
Cr	2.05	1.68	1.33	1.01	0.71
Cu	1.01	0.83	0.66	0.50	0.35
Hg	0.00	0.00	0.00	0.00	0.00
Ni	2.01	1.65	1.31	0.99	0.70
Pb	2.19	1.78	1.42	1.07	0.75
Zn	2.35	1.92	1.52	1.16	0.81
Naphthalene	0.00	0.00	0.00	0.00	0.00
Ester	17.68	14.45	11.50	8.70	6.10

7.4. ECOLOGICAL RISK ASSESSMENT

The risk characterization of ecological entities is based on dose response relationships. The estimated dose or exposure is compared with the response for each contaminant, which were established in Chapter 4. The following specific steps were performed in the ecological risk assessment:

1. The pore water exposure concentration (*EC*) for each contaminant was used as a representative dose for ecological entities (Table 7.9).

2. The response of the ecological system was determined from the lowest 10th percentile value on the *PNEC* empirical distribution function. The mean (μ_{10}) and standard deviation (σ_{10}) of response for each pollutant are provided in Chapter 4. The response values of each pollutant were used separately to determine ecological risk estimates.

3. Hazard or risk quotient (*HQ/RQ*) was calculated by dividing the exposure concentration distribution with the representative response distribution. *HQ* values greater than 1 represent adverse effects. If the value is less than 1, it means that at least 95% of ecological community is safe for 90% of the time (Sadiq et al., 2001d; Lenwood et al., 1998).

4. To estimate the probability of adverse effects according to the above criteria, the estimated *HQ* for each contaminant was converted into a corresponding risk value as suggested by Karman et al. (1996) and Thatcher et al. (1999) by the following relationship:

$$Risk = \int_{y=0}^{Ln(HQ)} \left[\frac{1}{S_m\sqrt{2\pi}} e^{\frac{(y-X_m)^2}{2S_m^2}} \right] \tag{7.1}$$

X_m = Average of the lognormally transformed data = 2.85;

S_m = Standard deviation of the lognormally transformed data = 1.74; and

y = Variable to describe the normal probability curve = $Ln\ (HQ)$

5. The risks estimated for each pollutant were grouped together as independent events according to the methodology discussed in Chapter 4, i.e.,

$$Risk\ (A + B) = Risk\ (A) + Risk\ (B) - Risk\ (A) \cdot Risk\ (B) \tag{7.2}$$

Similarly,

$$Risk\ (A + B + C) = Risk\ (A) + Risk\ (B) + Risk\ (C) - Risk\ (A) \cdot Risk\ (B) - Risk\ (B) \cdot Risk\ (C) - Risk\ (A) \cdot Risk\ (C) + Risk\ (A) \cdot Risk\ (B) \cdot Risk\ (C) \tag{7.3}$$

And so on. Thatcher et al. (1999) and Jooste (2000) have adopted similar methodologies in the case of multiple stressors.

6. The risk estimated from equation 7.1 is in the form of an empirical distribution function (EDF). Therefore composite ecological risks estimated from the series of equations (e.g. equations 7.2 and 7.3) are also in the form of an empirical distribution function.

The composite ecological risk values are reported in the form of minimum, maximum likely (mode, MLV) and maximum values. These risk parameters, i.e., minimum, MLV and maximum values were used to develop a triangular fuzzy number. Table 7.10 summarizes the minimum, MLV and maximum values for each discharge scenario, where these values represent the lowest 1%, mode and the highest 99% of the EDF (Jooste, 2001). The ecological risk varies over a wide range from 0.18 to 0.63 for the 10% discharge option, with an MLV of 0.26. It reduces to 0.04 to 0.33 for the 4% discharge option with an MLV of 0.13. The ecological risks estimated for different discharge scenarios are also compared in Figure 7.2.

Table 7.10: Composite ecological risks estimated for various discharge scenarios.

Discharge Scenario	Min.	MLV	Max.
10.0%	0.1775	0.2602	0.6276
8.5%	0.1366	0.2750	0.5542
7.0%	0.1175	0.2324	0.5035
5.5%	0.0678	0.1778	0.4244
4.0%	0.0448	0.1323	0.3302

The base of the triangular fuzzy number represents the uncertainty in the estimates. The apex of the triangle represents the most likely value. The highest uncertainty in the ecological risk estimates can be observed for the 10% discharge option and the least uncertainty is observed for the 4.0% discharge scenario.

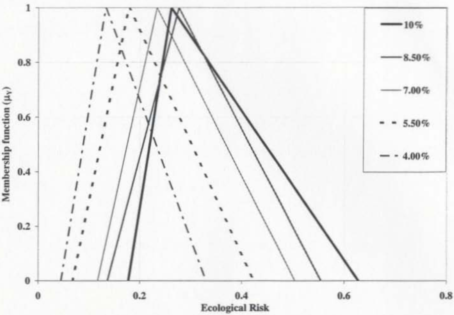

Figure 7.2. Ecological risk estimates for various discharge scenarios.

7.5. HUMAN HEALTH RISK ASSESSMENT

Human health is the other major components of environmental risk assessment. Human health risk assessment involves exposure through contaminated fish caught from the impacted site. Human health risk consists of cancer and non-cancer risk estimates. The chronic daily intakes (*CDI*) were calculated for each contaminant individually. For cancer risk, it was multiplied by the slope factor (*SF*) of arsenic (the only proven human carcinogen in this study) to estimate the unit risk over the life span of a person. Similarly, for estimation of non-cancer risks, reference doses (*RfD*) were divided by estimated *CDI* for each contaminant to determine *HI*. In the end, the *HIs* for all contaminants were summed up to determine the composite hazard index (HI_c). The following steps were performed to estimate the cancer and non-cancer human health risks:

1. The pore water exposure concentrations (*EC*) of each contaminant were employed to estimate the fish tissue concentrations, which were further used as human exposure concentrations through consumption of contaminated fish. The *CDI* was calculated for each contaminant separately (Chapter 5).

2. The cancer unit risk was estimated for arsenic only. The slope factor (*SF*) was multiplied by *CDI* to estimate the unit risk.

3. The reference doses (*RfD*) were used to estimate the non-cancer risks. The *CDI* was divided by corresponding *RfD* to estimate the *HI* for that contaminant.

4. The *HIs* for individual contaminants were added to get the composite hazard index (HI_c).

$$\sum HI = HI_c \tag{7.4}$$

The cancer and non-cancer risk estimates are reported in Table 7.11. The minimum, MLV and maximum values for various discharge scenarios are reported. The minimum values correspond to the lowest 1% and maximum values correspond to the highest 99th percentile value of the estimates, whereas the MLV is the highest frequency value, which corresponds to the mode value (Jooste, 2001).

Table 7.11. Human health risk assessment for various scenarios.

Items	Parameter	10.0%	8.5%	7.0%	5.5%	4.0%
Non-cancer (HI_c)	Min.	0.0065	0.0053	0.0043	0.0033	0.0024
	MLV	0.0163	0.0144	0.0135	0.0090	0.0048
	Max.	0.0856	0.0730	0.0624	0.0435	0.0326
Cancer (*Unit risk*)	Min.	1.24×10^{-16}	9.15×10^{-17}	8.26×10^{-17}	6.39×10^{-17}	4.53×10^{-17}
	MLV	5.54×10^{-16}	4.31×10^{-16}	5.18×10^{-16}	1.73×10^{-16}	1.87×10^{-16}
	Max.	3.49×10^{-15}	2.95×10^{-15}	2.35×10^{-15}	1.64×10^{-15}	1.16×10^{-15}

The highest value of HI_c for the 10% discharge scenario is approximately estimated to be 0.09. This value is approximately 12 times lower than the safety level of 1. Similarly, the unit risk values are very small, i.e., lower than *1 in a million*, which is conventionally used as a regulatory measure for human health risk assessment. Although all conditions represent safe situations from a human health risk viewpoint, the purpose of this study was to make a comparative evaluation of various discharge scenarios based on risk estimates. Therefore these values are used in the risk management section for comparing the different alternatives.

7.6. COST ESTIMATION

The second important component of risk management is the cost required to implement any given management alternative. The cost components considered in this study are treatment cost, cost of drilling fluid lost during discharge, ecological and human health damage costs (Chapter 6). To compare management alternatives or discharge options, the cost estimates are normalized over one year and values are reported in $/day. The summary of cost estimates for various discharge scenarios is given in Table 7.12.

Table 7.12. Cost ($/day) estimates for various discharge scenarios

Items ($/day)	Parameter	10.0%	8.5%	7.0%	5.5%	4.0%
Treatment cost	Min.	201.28	235.13	296.93	355.58	413.2
	MLV	352.79	437.25	452.06	540.48	586.68
	Max.	704.80	783.87	792.14	875.65	902.35
Ecological damage cost	Min.	26.71	20.56	17.68	10.20	6.74
	MLV	39.16	41.38	34.97	26.76	19.91
	Max.	94.44	83.40	75.77	63.86	49.69
Economic loss due to drilling fluid discharge	Min.	245.35	198.41	157.33	119.13	83.62
	MLV	338.92	274.08	217.33	164.56	115.51
	Max.	460.03	372.03	294.99	223.37	156.78
Human health damage cost		Negligible values of costs are estimated for cancer risk. The non-cancer risks costs are also neglected because the composites (HI_c) are less than 1 for all cases.				

The treatment cost was estimated from a regression model developed in Chapter 6. The values used for developing the treatment cost regression model were based on a one-month drilling time. The values estimated from regression models were divided by 12 to normalize over a period of one-year. In this regression model, the treatment cost is a function of percentage of base fluid attached. The uncertainties in the regression model coefficients contribute to the uncertainty in the treatment cost estimates. The minimum, MLV and maximum values are reported in Table 7.12. The minimum and maximum values correspond to 1st and 99th percentile values, respectively. These values were obtained after performing MC simulations on the treatment cost regression model.

The ecological damage cost was estimated based on the composite risk estimates. The ecological risks estimated in the total impact area of the oilfield were used as the probability of adverse effects on commercial fish. The following formulation was used to estimate the ecological damage due to a single well.

$$Ecological\ damage\ cost\ (\$/day) = \frac{ER \cdot Fish(kg/yr) \cdot Cost(\$/kg)}{365(days/yr) \cdot Wells} \tag{7.5}$$

where

ER = Composite ecological risk or probability of adverse effects

Fish caught = 2,110,000 kg/yr

Cost = 0.83 \$/kg (CEAA, 2001)

Total number of wells on the oilfield under study = 32

Conversion unit = 365 days/yr

The values estimated using the formulation above are summarized in Table 7.12. The other important component of cost estimation is the drilling fluid cost. The quantity of drilling fluid lost in each discharge scenario was converted into an economic loss by the following relationship.

$$Drilling\ fluid\ loss\,(\$/day) = \frac{Unit\ cost(\$/bbl)\cdot Drilling\ fluid\ volume(bbl)}{365\,(days)} \qquad (7.6)$$

where the unit cost of base fluid (ester) is reported in Chapter 6. The minimum. MLV and maximum values of ester unit cost are given in Table 6.5. The unit cost was defined by a triangular distribution T~ (251. 347. 471). The volumes of drilling fluid loss have already been estimated for each discharge option in Table 7.3. The unit costs were multiplied by the volume of ester lost in the corresponding discharge option and normalized over one-year. The economic loss for each discharge option was calculated and summarized in Table 7.12.

The last component of cost estimation is the human health damage cost. The human health cancer and non-cancer risks are used for estimating the cost of providing treatment facilities. The *HIc* values are below 1. therefore non-cancer risks can not be related to any treatment or hospitalization costs. Similarly the cancer risks values were too low to cause any significant expenditures for human health treatment. Therefore the values are not reported in Table 7.12.

The summary of total cost estimates in terms of minimum. MLV and maximum values are summarized in Table 7.13. The total cost values are also plotted in Figure 7.3 for the various discharge options. The total cost estimates vary over a wide range for the 10% discharge scenario. The daily cost estimated varies from 575 to 1230 $/day for a 10% discharge option over a year. The major contributor to the cost is the cost of drilling fluid lost. Contrary to that, for the 4% discharge scenario the major contributor to the total cost is the treatment cost. The total cost estimates show that for the 7.0%, 5.5% and 4.0% discharge options the range of total cost is approximately the same but an MLV for the 7.0% discharge scenario is less than the other scenarios (Figure 7.3).

Table 7.13. Total cost ($/day) estimates for various discharge scenarios

Parameter	10.0%	8.5%	7.0%	5.5%	4.0%
Min.	573.8	561.5	560.8	546.0	537.0
MLV	828.6	740.2	668.1	802.9	732.2
Max.	1230.6	1131.4	1075.5	1065.3	1079.0

7.7. TECHNICAL FEASIBILITY

The third attribute for the risk management study under consideration is the technical feasibility of the treatment options or management alternatives. The technical feasibility of various alternatives was defined based on three basic indicators: ease of operation (EO), status of the technology (ST), and control measures required (CM). These are not necessarily the only indicators to compare various treatment alternatives, rather they cover the basic information about each treatment option. For example, the ease of operation may include the total number of hours of operation, capacity of the treatment unit, and exposure of workers to drilling fluid. Similarly, the status of technology can encompass the efficiency of the treatment device, availability of skilled labor, and space requirements. The control measures include maintainability of the treatment units, and safety of workers. All of these sub-indicators need a detailed study to incorporate information from vendors, regulators and literature.

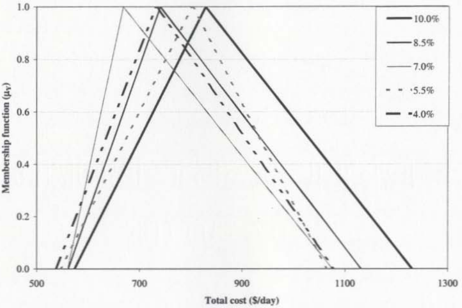

Figure 7.3. Total cost estimates for various discharge scenarios.

The technical feasibility basic indicators were defined qualitatively. Miller's scale (1965), in which five comparative scales are defined from 1 to 5 was used for this purpose. The highest number refers to the best level and the lowest one refers to the poorest. The levels 2, 3 and 4 refer to satisfactory, good, and very good, respectively. The numerical scores are assigned from 0 to 1. The scales are assumed as fuzzy numbers to incorporate vagueness and fuzziness in human judgement. The MLV of each scale represents the membership function of 1. The base of the fuzzy number represents uncertainty in human judgement. Figure 7.4 illustrates these five qualitative levels to compare technical feasibility basic indicators.

Based on Figure 7.4, the ST, EO and CM were rated for various discharge scenarios. As described before, this qualitative scaling needs significant information before assigning any scale. The present study does not focus extensively on this aspect of risk management. The scales were assigned based on a simple comparative evaluation. The scales 1 and 5 were not assigned for any indicator because the scale 1 represents a poor level, which is not the case for any alternative. Even in the case of ST, the scale 1 could not be assigned to the 10% discharge option, because it represents a current discharge practice in the U.S. offshore. Similarly, the scale 5 represents an excellent level, which could be assigned to EO in the case of the 10% discharge option or for the 4% discharge option for ST. It is avoided because there are some other technologies like thermal treatment, which were not evaluated in this study but might have a better scale rating. Based on these considerations, the scales were assigned to technical feasibility attributes for various discharge options as given below (Table 7.14).

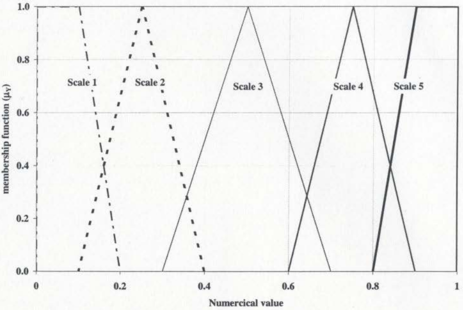

Figure 7.4. The qualitative scale used to rank technical feasibility indicators.

Table 7.14. The qualitative scales assigned to rank technical feasibility indicators.

Items	10.0%	8.5%	7.0%	5.5%	4.0%
Status of Technology (ST)	3	3	4	4	4
Ease of Operation (EO)	4	4	4	3	3
Control Measures Requirements (CM)	4	4	4	3	2

7.8. RISK MANAGEMENT - FUZZY COMPOSITE PROGRAMMING

7.8.1 NORMALIZATION OF BASIC INDICATORS

Fuzzy composite programming is used for a tradeoff analysis among conflicting objectives for different alternatives. Chapter 6 has provided a detailed step-by-step methodology for conducting fuzzy composite programming. Figure 7.5 provides a framework for determining a system improvement index to compare different discharge scenarios.

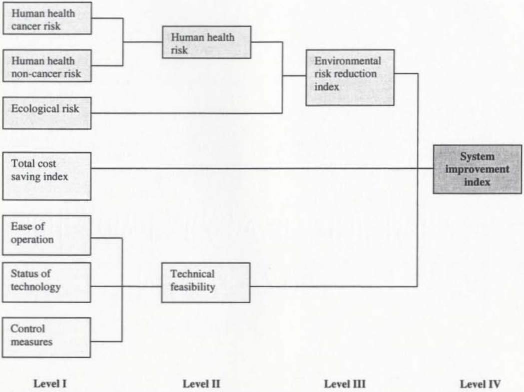

Figure 7.5. Framework for fuzzy composite programming for conducting tradeoff analysis among various discharge scenarios/management alternatives

The above figure shows that at the first level, the human health cancer and non-cancer risks were grouped together to make a human health risk index. Similarly the three basic indicators - ease of operation, status of technology, and control measures - were grouped to get the technical feasibility index. At the second level, the human health risk and ecological risk were grouped together to make a general group of the environmental risk reduction index. At the final stage, environmental risk reduction, technical feasibility and total cost saving indices were grouped to obtain a system improvement index. The values of the basic indicators used in fuzzy composite programming are given in Table 7.15.

The higher the risk value the less desirable that alternative will be. Similarly if the total cost is more, that option will not be desirable. But contrary to that if some basic indicator has a higher value (e.g., ease of operation), it may be considered a better option. To avoid this confusion, all basic indicators were normalized based on two criteria, either WORST > BEST (e.g., risk, cost etc.) or BEST > WORST (e.g., technical feasibility). These two criteria were used to normalize the basic indicators into unitless numbers scaling from 0 to 1. The method is discussed in detail in Chapter 6. The BEST and WORST values are selected among the estimated values for different discharge options. Table 7.16 lists the BEST and WORST values for all basic indicators.

After defining the BEST and WORST criteria values for each basic indicator, the values reported in Table 7.15 were normalized. All normalized basic indicator values are unitless and are scaled from 0 to 1, in which a higher value means a better option. Now the risk estimates are risk reduction index and total cost is converted into a cost saving index. Table 7.17 summarizes the normalized values of risk reduction and cost saving indices. The technical feasibility indicators have already been scaled from 0 to 1 so they will remain the same. The estimated normalized values of all basic indicators are reported in unitless terms so that they can be grouped according to composite programming methodology.

Table 7.15. Values of the basic indicators used in fuzzy composite programming.

Indicators	Values	10.0%	8.5%	7.0%	5.5%	4.0%
HHR_c	Min.	1.24×10^{-16}	9.15×10^{-17}	$8.26E \times 10^{-17}$	6.39×10^{-17}	4.53×10^{-17}
	MLV	5.54×10^{-16}	4.31×10^{-16}	5.18×10^{-16}	1.73×10^{-16}	1.87×10^{-16}
	Max.	3.49×10^{-15}	2.95×10^{-15}	2.35×10^{-15}	1.64×10^{-15}	1.16×10^{-15}
HHR_{nc}	Min.	0.0065	0.0053	0.0043	0.0033	0.0024
	MLV	0.0163	0.0144	0.0135	0.0090	0.0048
	Max.	0.0856	0.0730	0.0624	0.0435	0.0326
ER	Min.	0.1775	0.1366	0.1175	0.0678	0.0448
	MLV	0.2602	0.275	0.2324	0.1778	0.1323
	Max.	0.6276	0.5542	0.5035	0.4244	0.3302
Cost	Min.	573.8	561.5	560.8	546.0	537.0
	MLV	828.6	740.2	668.1	802.9	732.2
	Max.	1230.6	1131.4	1075.5	1065.3	1079.0
EO	Min.	0.60	0.60	0.60	0.30	0.30
	MLV	0.75	0.75	0.75	0.50	0.50
	Max.	0.90	0.90	0.90	0.70	0.70
ST	Min.	0.30	0.30	0.60	0.60	0.60
	MLV	0.50	0.50	0.75	0.75	0.75
	Max.	0.70	0.70	0.90	0.90	0.90
CM	Min.	0.60	0.60	0.60	0.30	0.10
	MLV	0.75	0.75	0.75	0.50	0.25
	Max.	0.90	0.90	0.90	0.70	0.40

Table 7.16. The criteria values used for normalizing basic indicators.

Parameter	Worst (W)	Best (B)	Criteria
Human Cancer Risk	3.49×10^{-15}	4.53×10^{-17}	W>B
Human Non-cancer Risk (HI_c)	2.40×10^{-3}	8.56×10^{-2}	W>B
Ecological Risk (ER)	6.28×10^{-1}	4.48×10^{-2}	W>B
Status of Technology	0.00	1.00	B > W Values are selected in qualitative terms from scales 1 to 5 and converted into numerical scores
Ease of Operation	0.00	1.00	
Control Measures Requirements	0.00	1.00	
Total Cost (\$/day)	1.231×10^{3}	5.37×10^{2}	W>B

7.8.2. WEIGHTING SCHEMES OF BASIC INDICATORS

After normalizing the basic indicators, the next step in fuzzy composite programming is to define the weights for different attributes. Double weighting schemes as described in Chapter 6 are used here. The first type of weighting (w) is based on one-to-one comparison of attributes. The AHP process is used to define the relative importance of each attribute and to group them into a generalized group. For example, human cancer risk and non-cancer risks were proportioned as 2:1 by importance, at the first level. Similarly, human health risk was given more priority than ecological risk by giving double weight to human health risk. At the highest level, the environmental risk reduction and cost saving were given three times more weight in comparison to the technical feasibility. The corresponding weights were calculated as

$$J = \begin{array}{c|ccc|c} & E & C & T & \\ \hline & 1 & 1 & 3 & E \\ & 1 & 1 & 3 & C \\ & 1/3 & 1/3 & 1 & T \end{array} \qquad (7.7)$$

Table 7.17. Normalized values of the basic indicators

Indicators	Values	10.0%	8.5%	7.0%	5.5%	4.0%
HHR_c (Reduction)	Min.	0.0000	0.1568	0.3309	0.5371	0.6764
	MLV	0.8523	0.8880	0.8628	0.9629	0.9589
	Max.	0.9772	0.9866	0.9892	0.9946	1.0000
HHR_{nc} (Reduction)	Min.	0.0000	0.1514	0.2788	0.5060	0.6370
	MLV	0.8329	0.8558	0.8666	0.9207	0.9712
	Max.	0.9507	0.9651	0.9772	0.9892	1.0000
ER (Reduction)	Min.	0.0000	0.1259	0.2129	0.3487	0.5103
	MLV	0.6304	0.6050	0.6781	0.7718	0.8499
	Max.	0.7723	0.8425	0.8753	0.9605	1.0000
Cost (Saving)	Min.	0.0000	0.1430	0.2236	0.2383	0.2186
	MLV	0.5796	0.7070	0.8110	0.6166	0.7186
	Max.	0.9469	0.9647	0.9657	0.9870	1.0000
EO	Min.	0.6000	0.6000	0.6000	0.3000	0.3000
	MLV	0.7500	0.7500	0.7500	0.5000	0.5000
	Max.	0.9000	0.9000	0.9000	0.7000	0.7000
ST	Min.	0.3000	0.3000	0.6000	0.6000	0.6000
	MLV	0.5000	0.5000	0.7500	0.7500	0.7500
	Max.	0.7000	0.7000	0.9000	0.9000	0.9000
CM	Min.	0.6000	0.6000	0.6000	0.3000	0.1000
	MLV	0.7500	0.7500	0.7500	0.5000	0.2500
	Max.	0.9000	0.9000	0.9000	0.7000	0.4000

A normalised matrix I was determined by normalising the matrix J column wise. The final weighted vector can be derived from summing the elements of each row of matrix I and normalising again for this vector.

$$I = \begin{bmatrix} 0.429 & 0.429 & 0.429 \\ 0.429 & 0.429 & 0.429 \\ 0.142 & 0.142 & 0.142 \end{bmatrix} \Rightarrow \begin{bmatrix} 1.288 \\ 1.288 \\ 0.429 \end{bmatrix} \tag{7.8}$$

After normalising to 1, the above equation becomes

$$W^T = [E \quad C \quad T] = [0.43 \quad 0.43 \quad 0.14] \tag{7.9}$$

where

E = Environmental risk (reduction);

C = Cost (saving); and

T = Technical feasibility

Table 7.18 summarises the calculated weights for all attributes at various levels. The second type of weight is the balancing factor (p). The balancing factor (p) was assigned to groups of indicators to show the importance of the maximal deviations. It represents the maximum difference of an indicator value from the best value for that indicator. The larger the value, the greater the concern with respect to the maximal deviation. When p = 1, all deviations are equally weighted, for p = 2, each deviation receives its importance in proportion to its magnitude (Torno et al., 1988).

7.8.3. TRADEOFF ANALYSIS

After assigning weights to basic indicators and more generalized groups at higher levels, a tradeoff analysis is performed. The analysis is performed for each management alternative or discharge option. The advantage of using fuzzy composite programming is that any two attributes can be compared while grouping, e.g., the environmental risk reduction index can be compared to the cost saving index or technical feasibility index.

Table 7.18. Weights estimated for basic indicators and more generalized groups

Indicators	Importance value	w	p
Human Cancer Risk	2	0.67	1
Human Non-cancer Risk	1	0.33	
Human Health Risk	2	0.67	2
Ecological Risk	1	0.33	
Status of Technology	1	0.33	2
Ease of Operation	1	0.33	
Control Measures Requirements	1	0.33	
Technical Feasibility	1	0.14	2
Environmental Risk Reduction	3	0.43	
Cost Saving	3	0.43	

Figure 7.6 shows a comparison of the environmental risk reduction and the cost saving indices for different discharge options. This plot shows the largest likely interval or range of the fuzzy number (base of the triangle, when membership function, $\mu(h) = 0$) in two dimensions. The x-axis shows the largest likely interval or range of the environmental risk reduction index and the y-axis shows the largest likely interval/range of the cost

saving index. For the 10% discharge option, the largest likely intervals are joined with the MLV. This can form a pyramid if it is shown in 3-D. The MLVs of two indices are also provided for each option given by the *x* and *y* components. The larger base of the pyramid shows higher uncertainty in the indices. The 10% discharge option has the largest base for the cost saving index. The 4% discharge option shows more uncertainty in cost saving index than the environmental risk reduction index. The MLV of cost saving and environmental risk reduction indices are at (0.93, 0.72). The ideal point in this type of comparison would be (1.0, 1.0) which is practically very difficult to achieve.

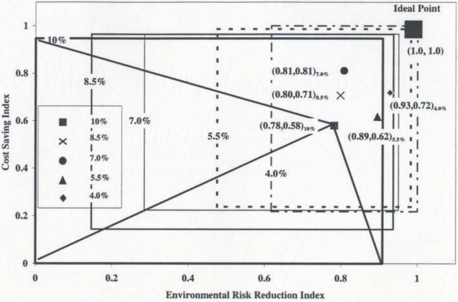

Figure 7.6. Comparison of environmental risk reduction and cost saving indices

The environmental risk reduction index can also be compared with the technical feasibility index. Figure 7.7 shows that the base (or largest likely interval) of the 5.5%

discharge option is larger than the other options, but the environmental risk reduction index uncertainty is maximum for the 10% discharge option. The 7.0% discharge option shows the best results from a technical feasibility viewpoint. If the system improvement index is based on only technical feasibility and environmental risk reduction viewpoints, then the 7.0% discharge option may be the best option. This can be observed, as its MLV is closest to the ideal point (1.0, 1.0). But this option shows higher uncertainty in the environmental risk reduction index than the 4.0% and 5.5% discharge options. The environmental risk reduction index was assigned three times more weight than the technical feasibility index, which reduces the chance of the 7.0% option to be selected as the best discharge option.

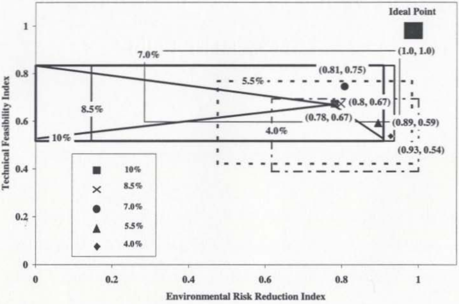

Figure 7.7. Comparison of environmental risk reduction and technical feasibility indices

Similarly, the cost saving index is also compared with the technical feasibility index. Figure 7.8 shows that the 7.0% option is the best option if the cost saving and the technical feasibility indices are the main criteria. The MLV of the 7.0% discharge option is closest to the ideal point (1.0, 1.0).

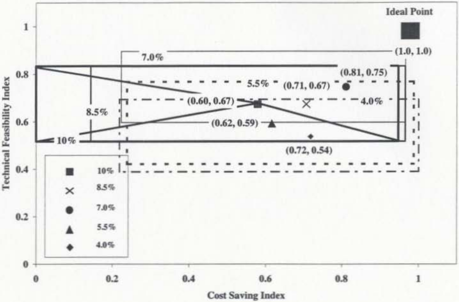

Figure 7.8. Comparison of cost saving and technical feasibility indices

After estimating the technical feasibility, cost saving and environmental risk reduction indices, they are grouped as a system improvement index. This final index is in the form of a fuzzy number. For all discharge options, the system improvement indices are compared in Figure 7.9. The ideal point of (1.0, 1.0) is also shown for comparison. The 7.0%, 5.5% and 4.0% discharge options look very close to each other. The MLV of the

7.0% and 4.0% discharge options are approximately the same, but the largest likely interval of the 7.0% discharge option is bigger than the 4.0% discharge option. The MLVs of the 7.0% and 4.0% discharge options are approximately 0.80, but the largest likely intervals of the 7.0% and 4.0% discharge options are in the range of 0.62 and 0.51, respectively. The larger base represents higher uncertainty in the estimates.

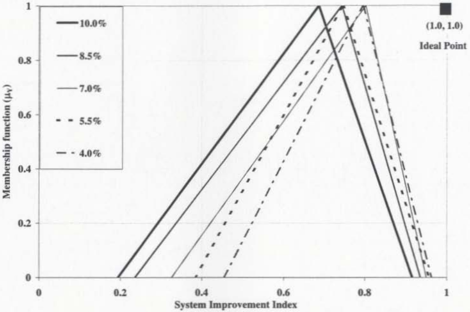

Figure 7.9. The system improvement index for comparison of various discharge options

7.8.4. RANKING ALTERNATIVES

Figure 7.9 shows that selection of the best alternative is not an easy task, because some alternatives are very close to each other. The Chen (1985) and Yager (1980b) centroidal index ranking methods were used to rank these discharge scenarios. In Chen's ranking method (1985) the utility value $U_i(x)$ was determined for each fuzzy number as described in Chapter 6. The highest utility value represents the best management alternative. Table 7.19 summarizes the system improvement index values for these discharge scenarios. The utility values and centroid were calculated for the system improvement index for each scenario. Similar conclusions can be drawn from both ranking methods that the 4.0% is the best management alternative and 7.0% is the next one and then followed by 5.5% discharge option.

Table 7.19. Ranking of various discharge scenarios

Alternatives	Min.	MLV	Max.	Yager (1980b) Centroid	Chen (1985) $U_i(x)$	Rank
10.0%	0.1935	0.6859	0.9154	0.6025	0.3634	5
8.5%	0.2354	0.7431	0.9353	0.6583	0.4698	4
7.0%	0.3259	0.8010	0.9496	0.7160	0.6437	2
5.5%	0.3829	0.7460	0.9573	0.7062	0.6280	3
4.0%	0.4534	0.7951	0.9630	0.7487	0.7208	1

7.8.5. SENSITIVITY ANALYSIS

The ranking of various discharge options was the last step in deciding which option is the best management alternative. The process of ranking alternatives involves assumptions and human judgments for assigning weights to various attributes. To confirm the ranking order achieved in the previous section, sensitivity analysis was performed in which various weighting schemes were employed and the entire fuzzy composite programming procedure was repeated. Table 7.20 summarizes the trials in which new weights and importance values were assigned to the last three groups. The first trial results have already been discussed in which risk reduction and cost saving indices were given three times more weight than the technical feasibility index. The second trial represents the case, in which technical feasibility is not considered, rather risk reduction and cost saving indices were assumed to be the selection criteria for the best management alternative. Similarly in the third trial, the environmental risk reduction index was given 1.5 times more weight than the cost saving index. This trial represents the pro-environment scenario. In the last trial, the weights of environmental risk reduction and cost saving indices are reversed, which is a pro-cost saving scenario.

Table 7.20. Different weighting schemes for sensitivity analysis.

Trials	Weighting schemes	Environmental risk reduction index	Cost saving index	Technical feasibility index
Trial 1 Risk and cost having same weights	Importance value	3	3	1
	w	0.43	0.43	0.14
	p	2		
Trial 2 Risk and cost having same weights	Importance value	1	1	0
	w	0.50	0.50	0.00
	p	2		
Trial 3 Risk is having more weight than cost	Importance value	3	2	1
	w	0.50	0.33	0.17
	p	2		
Trial 4 Cost is having more weight than risk	Importance value	2	3	1
	w	0.33	0.55	0.17
	p	2		

The second trial results are plotted in Figure 7.10. The 5.5% option improves its ranking from third to second position. The 7.0% option was at second position in the trial due to its better technical feasibility index value. The 4.0% discharge option is again shown to be the best discharge option among all alternatives. Both ranking methods have provided the robust ranking rating order.

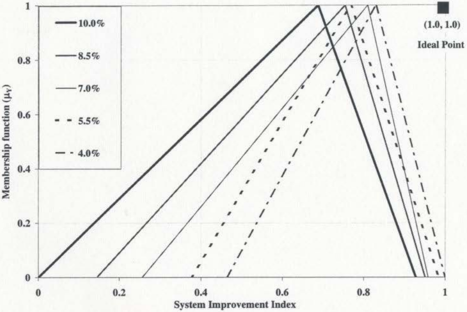

Figure 7.10. The system improvement index for comparison of various discharge options for trial 2

The third trial represents the situation in which environmental reduction index is given more weight than cost saving index and represents a pro-environment scenario. The environmental risk reduction index is maximum for the 4.0% discharge option. Therefore a utility index of the 4.0% discharge option is improved from 0.72 to 0.74, approximately. The ranking orders show that the 4.0% discharge option is the best option and 5.5% is second, followed by the 7.0% discharge option, although the second and third ranks have no appreciable differences in their utility and centroidal values. The 10.0% discharge option is the least desirable option among all management alternatives. Figure 7.11 shows the system improvement indices for all management alternatives.

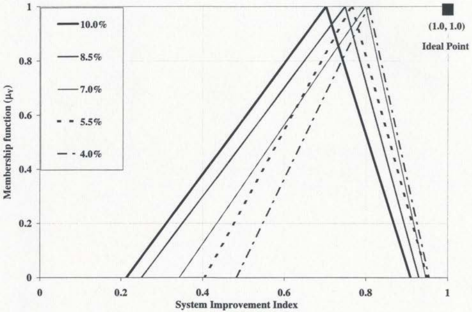

Figure 7.11. The system improvement index for comparison of various discharge options for trial 3

The final trial is a pro-cost saving scenario in which the cost saving index is given 1.5 times more weight than the risk reduction scenario. The results show that the 4.0% discharge option is still the best management alternative but the 7.0% has improved its ranking again from 3 to 2 in comparison to the 5.5% discharge scenario. The utility value of 7.0% discharge scenario is appreciably higher than the 5.5% discharge alternative. The 10.0% discharge option is still the least desirable option, then followed by the 8.5% discharge option. Figure 7.12 compares the system improvement indices for all management alternatives.

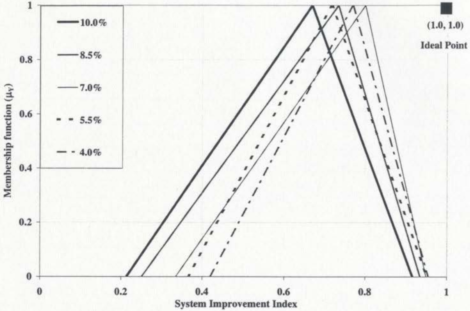

Figure 7.12. The system improvement index for comparison of various discharge options for trial 4

A summary of the ranking for various weighting schemes is provided in Table 7.21. Overall, the 4.0% discharge option is the best management alternative. The second best option lies somewhere between the 5.5% and 7.0% discharge options. The least desirable option is the current practice followed in the U.S. jurisdictions (Gulf of Mexico, California, and Alaska). The better management alternatives are those options in which treatment technology is sophisticated enough to substantially reduce the ecological damages without compromising the cost of treatment.

Table 7.21. Summary of sensitivity analysis results for ranking management alternatives.

Trials	Method	10.0%	8.5%	7.0%	5.5%	4.0%
Trial 1 Risk and cost having same weights	$U_t(x)$	0.3634	0.4698	0.6437	0.6280	0.7208
	Centroid	0.6025	0.6583	0.7160	0.7062	0.7487
	Rank	5	4	2	3	1
Trial 2 Risk and cost having same weights	$U_t(x)$	0.3789	0.5948	0.7192	0.7273	0.8074
	Centroid	0.5751	0.6503	0.7078	0.7225	0.7774
	Rank	5	4	3	2	1
Trial 3 Risk is having more weight than cost	$U_t(x)$	0.3684	0.4680	0.6437	0.6515	0.7426
	Centroid	0.6137	0.6628	0.7183	0.7190	0.7596
	Rank	5	4	3	2	1
Trial 4 Cost is having more weight than risk	$U_t(x)$	0.3563	0.4562	0.6362	0.5755	0.6655
	Centroid	0.5992	0.6564	0.7169	0.6856	0.7246
	Rank	5	4	2	3	1

On the East Coast of Canada, the regulations concerning drilling cutting discharges are currently being reviewed. A reduction from 15% attached base fluid to the neighborhood of say 7.0 to 8.0% of dry weight of cuttings corresponds to approximately 12.0% to 5 - 6% of wet cuttings. The results of this study shows that a discharge scenario of 5 - 6 % (wet cuttings) is one of the better management alternative, if not the best.

Chapter 8

CONCLUSIONS AND RECOMMENDATIONS

This chapter first presents some conclusions based on methodologies developed for contaminant fate modeling, ecological and human health risk assessments and risk management. It also summarises some specific conclusions based on a hypothetical case study of an oilfield on the East Coast of Canada. This chapter also provides recommendations and establishes the directions for future research. At the end, a statement of originality of this thesis is presented.

8.1. SUMMARY AND CONCLUSIONS

The study was carried out by adopting a holistic approach for risk management of offshore petroleum drilling waste discharges in the marine environment. The research focused on the following objectives: (1) development of probabilistic contaminant fate models using fugacity and aquivalence based approaches for organic compounds and heavy metals, respectively; (2) development of an ecological risk assessment methodology using probabilistic concepts; (3) development of human health cancer and non-cancer risk assessment methodologies using probabilistic concepts; (4) development of a fuzzy composite framework for risk management by integrating environmental risk assessment with cost estimation and technical feasibility of various treatment options; and (5) application of a risk management framework for a hypothetical case study of drilling waste discharges on the East Coast of Canada.

Keeping these objectives in perspective, the following are the conclusions of this research:

1. A new methodology for contaminant fate modeling using a chemical specific approach was proposed in Chapter 3. Steady state non-equilibrium fugacity/aquivalence based equations were used to estimate the distributions of concentration in the water column (C_w) and sediment pore water (C_{PW}). The uncertainty and variability in the model inputs were expressed by their statistical distributions. The C_w and C_{PW} were estimated using Latin Hypercube Sampling (LHS) based Monte Carlo (MC) simulations. The fate model outputs, C_w and C_{PW} followed the lognormal distribution due to the multiplicative nature of the model. The parameters of the lognormal distributions LN ~ (μ, σ) were estimated for different discharge conditions, based on pollutant loading rates (E) and impact radii (R). The estimated parameters of the lognormal distribution (μ, σ) for known discharge conditions were used for performing multiple regression analyses. The highest 95th percentile was used as the predicted environmental concentration (*PEC*). The uncertainties in the 95th percentile values (*PEC*) were estimated by the coefficients of mean (μ) and standard deviation (σ) regression models. The methodology developed for estimating *PEC* through regression models is flexible and can be easily modified

to any other desired safety level depending on the management goals and objectives. The strength of this methodology is that it incorporates natural variabilities and/or uncertainties in the model input parameters, which help in predicting the output concentrations and their associated uncertainties. This approach did not consider the model uncertainty, which is generally not high in well-tested models (CCME, 1997). The developed methodology is not only applicable to drilling waste discharges, rather it can be used for other industrial wastes having known physico-chemical characteristics.

2. A comprehensive methodology for probabilistic ecological risk assessment was developed in Chapter 4. The whole ecological community was defined as assessment endpoints. The toxicity data (LC_{50}, EC_{50} and *NOEC*) were converted into predicted no effect concentrations (*PNEC*). The lognormal was found to be the representative distribution for *PNEC* data. The lowest 10th percentile of the *PNEC* distribution was defined as the safety level or *PNEC* criteria value. Bootstrapping was performed on original *PNEC* data to determine uncertainty in the *PNEC* criteria values. The exposure assessment was based on contaminant fate modeling results. The estimated *PEC* values were converted into exposure concentrations (*EC*) by adjusting for bioavailability (*BF*) and probability of exposure (p). The hazard or risk quotients (*HQ/RQ*) were calculated by taking the ratio of *EC* and *PNEC* criteria values. The CHARM model's approach (Thatcher et al., 1999) was used to convert *HQ/RQ* into risk estimates for each contaminant. The composite ecological risk for drilling waste was determined by integrating the individual risk estimates assuming statistically

independent events. The ecological risk assessment methodology developed is unique and allows for the incorporation of more toxicity data (as it becomes available) to improve *PNEC* criteria values. This technique can be very useful in developing risk based water and/or sediment quality criteria. By fixing an acceptable risk posed by a particular pollutant in water and/or sediments, the pollutant load can be estimated to determine its allowable level in the industrial discharges. This risk based approach can help in developing pollutant effluent and emission standards.

3. A risk assessment methodology for human health was developed in Chapter 5. The human health risk methodology was based on the consumption of contaminated seafood. The chronic daily intake rate (*CDI*) was established based on fish ingestion rates, lipid content of contaminated fish, bioconcentration factors, exposure duration, exposure frequency, and averaging time. The input parameters were defined by triangular distributions based on the ranges and maximum likely values (MLV) reported in the literature. The human health risk assessment methodology for drilling waste discharges adopts a probabilistic approach based on an extensive literature search for input parameters. A comparison of the U.S. EPA (2000a) and the present study methodologies for human health risk assessment of drilling waste discharges was also presented in this chapter. The developed methodology is more comprehensive and extensive than the traditional U.S. EPA's (2000a) deterministic approach for drilling waste discharges.

4. A risk management methodology using fuzzy composite programming (CP) was developed in Chapter 6. The fuzzy composite programming involved identification of basic indicators, a methodology for grouping basic indicators, weighting schemes, converting linguistic terms and statistical data into fuzzy numbers, and ranking methodologies for management alternatives. To perform tradeoff analysis for the selection of the best management alternative or discharge scenario, cost estimates and technical feasibility parameters were studied in this chapter. A linear regression model was developed for the estimation of treatment cost as a function of percent base fluid attached to the wet drill cuttings. The basic indicators - risk estimates, technical feasibility, and cost estimates - were defined by triangular fuzzy numbers to incorporate their uncertainties. The final utility and centroidal values of the system improvement indices were calculated through Chen (1985) and Yager (1980b) ranking methods, respectively to determine the ranking order of the management alternatives. The CP methodology has successfully been used in other environmental engineering problems (e.g., Stansbury et al., 1989). In the present research, CP methodology is modified for probabilistic quantitative and fuzzy qualitative data. This approach has never been applied for management of drilling waste discharges. This modified CP methodology is also applicable to other environmental decision-making problems.

5. The framework of risk management developed in the first six chapters was applied to a hypothetical case study on the East Coast of Canada in Chapter 7. Five discharge scenarios were defined based on the percent base fluid attached to the wet drill

cuttings. These discharge scenarios or management alternatives were 10.0%, 8.5%, 7.0%, 5.5% and 4.0% attached base fluids. The regression models developed in Chapter 3 were used to estimate the *PEC*, which were converted into exposure concentrations using *BF* and *p*. The exposure concentrations were used in the human and ecological probabilistic risk assessment models to quantify the risk values. Similarly, cost estimates for treatment, drilling fluid lost, and ecological and human health damages for different discharge scenarios were made. The technical feasibility parameters - status of the technology, ease of operation and control measures required - were defined in qualitative terms. The qualitative terms were converted into numerical scores using Miller's scale (1965). The importance matrix of basic indicators was developed using an analytical hierarchy process (AHP). A double weighting scheme was employed in CP. All basic indicators were grouped into environmental risk reduction, cost saving and technical feasibility indices to perform a tradeoff analysis. The 4% attached base fluid option was the best management option for the first trial when risk and cost were given equal weight and technical feasibility was allotted one-third of the weight. The 7.0% discharge option was the second best management alternative and that was followed by 5.5%, 8.5% and 10.0%, respectively. The sensitivity analysis was performed using different weighting schemes to account for human subjectivity. In the second trial, the technical feasibility was not included in determining the system improvement index. The 4.0% discharge option remained the best management alternative, but the 5.5% discharge option improved its ranking from 3 to 2, and 7.0% discharge option moved to 3rd place. The 3rd trial was designed as a pro environment scenario in which risk reduction was given 1.5 times more weight than the cost saving index. The technical feasibility was given one-third importance in comparison to environmental risk. The overall ranking remained the same as that of the second trial. The last trial was a pro cost-saving scenario in which the relative importance of the 3rd trial was reversed for the cost and the risk indices. Now again, the 4.0% discharge option remained the best management alternative, but the 7.0% discharge option improved its ranking from 3 to 2, and the 5.5% discharge option ranking dropped from 2nd to 3rd place. The 10.0% option remained the least desirable discharge option. It was concluded that the 4.0% was the best management alternative for the discharge of drilling waste in the marine environment. The other better management alternatives or discharge options were the 7.0% and/or 5.5% attached base fluid to the wet cuttings. This case study illustrated the utility of the methodologies developed in first six chapters of this thesis. This case study provided a framework for a decision support system for the selection of the best drilling waste marine discharge option under any known regulatory and technical constraints.

8.2. RECOMMENDATIONS

Recommendations are useful for setting the directions of future research. The following recommendations are presented based on the limitations and problems faced during this study:

1. The present study used MC simulations for the probabilistic analyses to incorporate uncertainty in the input parameters. To avoid the assumption of independent input variables, interval analysis and probability bound analysis may be used. Risk Calc (1999) at present is only capable of handling simple mathematical formulations. In the present research, effort was made to apply these methods in the beginning, but they did not work properly due to complexities in the contaminant fate modeling and ecological risk assessment models. In the future research, it may be very useful to develop a methodology for contaminant fate modeling and ecological risk assessment using fuzzy numbers to incorporate the uncertainty in the input variables and compare with the results of MC simulations.

2. The fugacity/aquivalence based model inputs are defined by statistical distributions. A probabilistic parametric approach was employed to perform the analysis. The inputs were assumed to be independent of each other due to the lack of reliable data to develop a correlation among input variables. For future studies, more data need to be collected to define the relationships among input variables to perform MC simulations.

3. The methodology of ecological risk assessment was based on defining the whole ecological community as the assessment endpoints. The criteria *PNEC* values or safety levels were developed based on available data and information from various sources. The criteria *PNEC* values will be changed if more comprehensive toxicity response information becomes available. There is an immediate need for developing a

database for toxicity response of organisms (e.g., LC_{50}, $NOEC$) for different contaminants, which should be made available to the public domain.

4. The bioavailability of contaminants is a sensitive issue in ecological and human health risk assessment. The bioavailability (BF) was defined by leaching or conversion factors in this study (U.S. EPA, 2000a). More research and laboratory experiments are needed in this direction to estimate the actual bioavailable fraction of the contaminants.

5. The fugacity/aquivalence models developed in this study were based on an assumption of steady state conditions. It may be useful to modify the fugacity/aquivalence based models by introducing a time factor into the formulation for unsteady state solution.

6. A chemical specific approach was used in this study due to the lack of physico-chemical and toxicity data of drilling waste as a whole (or a single entity). A whole toxicity approach can be used in future if enough information and data becomes available.

7. The exposure concentrations were a function of exposure probability (p), which was calculated by the ratio of impact area (A_w) to the total area under study. The migration rates of fish may play a very important role in estimating the actual exposure to the

contaminants. When more information is available in specific studies, it can be employed for more realistic estimates of exposure probability.

8. Human health risks were estimated based on the consumption of contaminated fish due to drilling waste discharges into the marine environment. The other source of human health exposure is the drilling platform, where workers are exposed to chemicals through inhalation, ingestion and dermal contact. That aspect of drilling waste was not considered in the present study and can be incorporated in future research for risk management of drilling waste.

9. The technical feasibility of various treatment options was defined by three parameters: status of the technology, ease of operation and control measures. These parameters were defined by five qualitative fuzzy scales that ranged from the best to the poorest. A more comprehensive study could be used for this aspect of the research.

10. The cost estimates were based on treatment, drilling fluid loss and human and ecological damage costs in the present study. The costs related to non-water quality impacts, including global warming impacts (GWI), ozone depletion potential (ODP) and risks associated with the safety issues at the platform can also be incorporated into the analysis.

11. The environmental impact component of this research was focussed on the risks associated with ecological and human health due to exposure through discharges of drilling waste into the marine environment. This study did not estimate the GWI, ODP and risks related to the health and safety (H&S) of the workers. A life cycle analysis (LCA) type of approach could be an alternative solution in which cradle-to-grave or cradle-to-gate type of methods can be used over the life span of drilling waste. The LCA could start from a factory where drilling fluids are manufactured to their final disposal location or a recycling facility.

8.3. STATEMENT OF ORIGINALITY

Originality in the present research can be viewed from following perspectives:

Fugacity/aquivalence based models are used extensively in lake and river systems in the deterministic mode. In this research, a probabilistic framework for conducting contaminant fate modeling was presented for a marine environment. The output concentrations (C_{w}, C_{PW}) were lognormally distributed and the parameters of the distributions were converted into empirical regression models. The regression models were grouped together to estimate *PEC*, which was defined by the highest 95th percentile value. It can be defined at any level based on the management goals and objectives. These *PEC* equations are flexible and can easily be modified to any desired exposure level.

A new methodology for ecological risk assessment was developed for drilling waste discharges using the U.S. EPA (1998) and CCME (1999) frameworks. A new procedure for streamlining the LC_{50} and *NOEC* data into *PNEC* values was introduced. The *PNEC* data for different organisms were found to be lognormally distributed. The selection criteria of endpoints in the CHARM model (Thatcher et al., 1999) are based on only three types of organisms: fish, algae and crustaceans, whereas in the current study the whole ecological community was defined as endpoints. The criteria *PNEC* values or safety levels were estimated using bootstrapping to incorporate the uncertainties in the estimates. The safety level (*HQ*/*RQ*) of 1 or less was designated to correspond to the protection of 90% of the species 95% of the time.

Most of the studies related to drilling waste discharges in the marine environment (e.g., U.S. EPA, 2000a, 1999a; Meinhold, 1998) define the acceptable pollutant levels in a drilling waste stream based on water quality standards and guidelines proposed by regulatory agencies. Recently, the author and coworkers (Sadiq et al., 2001d) have proposed a methodology for evaluating various regulatory drilling waste discharge options based on the toxicity response of the whole ecological community using the approach developed in this thesis.

In this study, results of contaminant fate modeling were integrated with probabilistic human health risk assessment using LHS based MC simulations. The probabilistic human health risk assessment approach is not new but in the present study, an extensive literature search was conducted to estimate the parameters of the proposed triangular distributions of human health risk assessment through consumption of contaminated fish.

New simple techniques for estimating the costs of treatment. ecological and human health damages were introduced in this study. Probabilistic data were converted into triangular fuzzy numbers using confidence intervals and modes of the risk and cost distributions. The risk management methodology of fuzzy composite programming has been used previously in environmental engineering related problems. but has never been applied to drilling waste discharges. A risk management study encompassing risk minimization. cost saving and technical feasibility of discharge options. has never been studied for drilling waste management.

This study introduced a new concept of integrating probabilistic fate modeling with ecological and human health risk assessment methodologies within a risk management framework to determine the ranking order of management alternatives under these conflicting objectives. This study has provided a framework for a decision support system for the selection of the best drilling waste marine discharge option under any set of regulatory and technical constraints.

REFERENCES

Adamo, J. M. (1980). Fuzzy Decision Trees, *Fuzzy Sets and Systems*, 4 (3): 207-220.

Ang, A. H-S and Tang, W. H. (1984). *Probability Concepts in Engineering Planning and Design*, Volume II: Decision, Risk and Reliability, John Wiley & Sons.

Anon (1999). *Shale Shakers and Drilling Fluid Systems: Techniques and Technology for Improving Solids Control Management*; American Association of Drilling Engineers, Gulf Publishing Company.

ASTM (1998). *Technical and Professional Training*, RBCA Fate and Transport Models: Compendium and Selection Guidance, www.astm.org.

Atchison, G. J., Murphy, B. R., Bishop, W. E., McIntosh, A. W., and Mayes, R. A. (1977). Trace Metal Contamination of Bluegill (*lepomis macrochirus*) from Two Indiana Lakes, *Transactions, American Fisheries Society*, 106 (6): 637-640.

Australian and New Zealand Guidelines for Fresh and Marine Water Quality (1999). *National Water Quality Management Strategy*, Australia and New Zealand Environment and Conservation Council.

Baas, S. M, and Kwakernaak, H. (1977). Rating and Ranking of Multiple Aspect Alternative using Fuzzy Sets. *Automatica*, 13: 47-58.

Baldwin, J. F., and Guild, N. C. (1979). Comparison of Fuzzy Sets on the Same Decision Space, *Fuzzy Sets and Systems*, 2 (2): 213-231.

Bardossy, A., Bronstert, A., and Merz, B. (1995). 1-, 2- and 3-Dimensional Modeling of Groundwater Movements in the Unsaturated Soil Matrix using a Fuzzy Approach, *Advances in Water Resources*, 18(4): 237-251.

Bellman, R., and Zadeh, L. A. (1970). Decision-Making in the Fuzzy Environment, *Management Science*, 17B (4): 141-164.

Benjamin, J. R., and Cornell, C. A. (1970). *Probability, Statistics, and Decision for Civil Engineers*, McGraw-Hill Company.

Benoit, D. A., Leonard, E. M., Christensen, G. M., and Fiandt, J. T. (1976). Toxic Effects of Cadmium on Three Generations of Brook Trout (*salvelinus fontinalis*). *Transaction, American Fisheries Society*, 105 (2): 358-550.

Bernhard, T. (2000). *Metals Bioavailability in the Navy's Tiered Ecological Risk Assessment Process*, Washington Navy Yard.

BESTFIT (1993). Palisade Corporation. N.Y. U.S. 14867.

Bogardi, I. and Bardossy, A. (1983). Application of MCDM to Geological Exploration. In: *Essays and Surveys on Multiple Criterion Decision-Making*, Henson, P. (Editor), Springer-Verlag, NY.

Bonnisone, P. P. (1980). A Fuzzy Set Based Linguistic Approach: Theory and Applications. *Proceedings of the 1980 Winter Simulation Conference*, Orlando, Florida, pp. 99-111.

Bonnisone, P. P. (1982). A Fuzzy Sets Based Linguistic Approach: Theory and Applications. In: *Fuzzy Information and Decision Processes*, Gupta, M. M., and Sanchez, E. (Editors), North-Holland, pp. 329-339.

Booman, C. and Foyn, L. (1996). Effects of the Water Soluble Fraction of Crude Oil on Marine Fish Larvae and Crustaceans, In: *Produced Water 2*: Environmental Issues and Mitigation Technologies, M. Reed and S. Johnsen (Editors), *Environmental Science Research*, Vol. 52, Plenum Press, New York.

Boudou, A., and Ribeyre, F. (1984). Influence of Exposure Length on the Direct Bioaccumulation of Two Mercury Compounds by *Salmo gairdneri* and Relationship between Organism Weight and Mercury Concentrations, *Water Research*, 8 (1): 81-86.

Brandsma, M. G. (1996). Computer Simulations of Oil-Based Mud Cuttings Discharges in the North Sea. In: *The Physical and Biological Effects of Processed Oily Drill Cuttings*, E & P Forum Report No. 2.61/202, pp. 25-40.

Brans, J. P., Mareshal, B. and Promethee (1984). A New Family of Outranking Methods in Multi Criteria Analysis, In: J. P. Brans (Editor), Operational Research '84. North Holland Amsterdam, (*Proceedings of the Tenth IFORS International Conference on Operational Research, Washington, D. C.*), pp. 477-490.

Britannica (2001). http://www.britannica.com.

Broderius, S. J. (1991). Modeling the Joint Toxicity of Xenobiotics to Aquatic Organisms: Basic Concepts and Approaches. In: *Aquatic Toxicity and Risk Assessment*: 14th volume, Mayes, MA; Barron, MG, Eds. ASTM STP 1124, Philadelphia, PA: American Society of Testing Materials, pp. 107-127.

Brody, M; Conner, W, Pearlstine, L, and Kitechens, W. (1989). Modeling Bottom land Forest and Wildlife Habitat Changes in Louisiana's Atchafalaya Basin, In: *Freshwater Wetlands and Wildlife*, Sharitz, RR; Gibbons, JW, Eds., U.S. Department of Energy Symposium Series, No. 61. CONF-8603100, Oak Ridge, TN: Office of Science and Technical Information, U. S. D. O. E.

Brody, MS, Troyer, ME, Valette, Y. (1993). Ecological Risk assessment Case Study: Modeling Future Losses of Bottomland Forest Wetlands and Changes in Wildlife Habitat Within A Louisiana Basin, In: *A Review of Ecological Assessment Case Studies From a Risk Assessment Perspective*, Washington, D.C., Risk Assessment Forum, U. S. EPA, pp. 12-1 to 12-39. EPA/630/R-92/005.

Buckley, J. J. (1984). The Multiple-Judge, Multiple Criteria Ranking Problem: A Fuzzy Set Approach, *Fuzzy Sets and Systems*, 13 (1): 25-38.

Buckley, J. J. (1985). Fuzzy Decision-Making with Data, Application to Statistics, *Fuzzy Sets and Systems*, 16 (2): 139-147.

Buckley, J. J., and Chanas, S. (1989). A First Method of Ranking Alternatives Using Fuzzy Numbers (Short Communications), *Fuzzy Sets and Systems*, 30 (3): 337-339.

Buikema, A. L., Jr. Heath, A G., and Parker, B. C. (1982). Biological Monitoring, Part IV - Toxicity Testing, *Water Research*, 16: 239-262.

Burmaster, D. E., and Hull, D. A. (1996). Using Lognormal Distributions and Lognormal Probability Plots in Probabilistic Risk Assessments, *Human and Ecological Risk Assessment*, 3 (2): 235-255.

Campbell, P. G. C., Lewis, A. G., Chapman, P. M., Crowder, A. A., Fletcher, W. K., Imber, B., Luoma, S. N., Stokes, P. M., and Winfery, M. (1988). *Biologically Available Metals in Sediments*, NRCC No. 27694. National Research Council of Canada, Ottawa, Canada.

Campfens, J., and Mackay, D. (1997). Fugacity-based Model of PCB Bioaccumulation in Complex Aquatic Food Webs, *Environmental Science & Technology*, 31: 577-583.

Canadian Council of Ministers of Environment, CCME (1997). *A Framework for Ecological Risk Assessment*: Technical Appendices, PN1274.

Canadian Council of Ministers of Environment, CCME (1999). *Canadian Water Quality Guidelines*, Summary Table.

Canadian Environmental Assessment Agency, CEAA (2001). www.ceaa.gc.ca.

Candler, J. R. and Leuterman, A. J. J. (1997). Effectiveness of a 10-Days Amphipod Sediment Test to Screen Drilling Mud Base Fluids for Benthic Toxicity, *Society of Petroleum Engineers*, SPE 37890.

Chen, S. H. (1985). Ranking Fuzzy Numbers with Maximising Set and Minimising Set. *Fuzzy Set Systems*, 17(2): 113-129.

Chen, S. J., and Hwang, C L. (1992). *Fuzzy Multiple Attribute Decision-Making*, Springer-Vaerlag, NY.

Chen, S. J., and Hwang, C. L. (1989). Fuzzy Scoring of Fuzzy Number - A Direct Comparison Index, *Unpublished Paper*.

Cheng, Y. M., and McInnis, B. (1980). An Algorithm for Multiple Attribute, Multiple Alternative Decision Problem Based on Fuzzy Sets with Application to Medical Diagnosis, *IEEE Transactions on System, Man and Cybernatics*, 20 (3): 645-650.

Civanlar, M. R., and Trussell, H. J. (1986). Constructing Membership Functions using Statistical Data, *Fuzzy Set Systems*, 18 (1): 1-13.

CNOPB (2001). *Canada-Newfoundland Offshore Petroleum Board*, www.cnopb.nfnet.com

Covello, V. T. and Merkhofer, M. W. (1993). *Risk Assessment Methods: Approaches for Assessing Health and Environmental Risk*, Plenum Press, New York.

Crow, E. L., and Shimizu, K., Eds. (1988). *Lognormal Distributions, Theory and Applications*, Mercel Dekker, N. Y.

Cullen, A. C., and Frey, H. C. (1999). *Probabilistic Techniques in Exposure Assessment: A Handbook for Dealing with Variability and Uncertainty in Models and Inputs*. Plenum Press: New York, 352 pp.

Daan, R. K, Booij, M. M. and Weerlee, E, Van. (1996). Environmental Effects of a Discharge of Cuttings Contaminated with Ester-Based Drilling Muds in North Sea, *Environmental Toxicology and Chemistry*, 15 (10): 1709-1722.

Delgado, M., Verdegay, J. L., and Vila, M A. (1988). A Procedure for Ranking Fuzzy Numbers Using Fuzzy Relations, *Fuzzy Sets and Systems*, 26 (1).

Deutch, B., Borg, B., Kloster, L. Meyer, H., and Moller, M. M. (1980). The Accumulation of ^{65}Zn by Various Marine Organisms, *Ophelia (Suppl.)*, 1: 235 - 240.

Diamond, M. (1999). Development of a Fugacity/Aquivalence Model of Mercury Dynamics in Lakes, *Water, Air and Soil Pollution*, 111: 337-357.

Diamond, M., Mackay, D., Poulton, D. and Stride, F. (1994). Development of a Mass Balance Model of the Fate of 17 Chemicals in the Bay of Quinte, *Journal of Great Lakes Research*, 20: 643-666.

Dingman, S. L., and Sharma, K. P (1997). Statistical Development and Validation of Discharge Equations for Natural Channels, ASCE, *Journal of Hydrology*, 199: 13-35.

Dou, C., Woldt, W., Bogardi, I., and Dahab, M. (1995). Steady State Groundwater Flow Simulation with Imprecise Parameters, *Water Resources Research*, 31 (11): 2709-2719.

Duah, D. K. (1993). *Hazardous Waste Risk Assessment*, Lewis Publishers.

Dubois, D. and Prade, H. (1982). The Use of Fuzzy Numbers in Decision Analysis, In: *Fuzzy Information and Decision Processes*, Gupta, M. M., and Sanchez, E. (Editors), North-Holland, pp. 309-321.

Dubois, D., and Prade, H. (1983). Ranking of Fuzzy Numbers in Setting the Possibility Theory, *Information Sciences*, 30: 183-224.

Dubois, D., and Prade, H. (1986). Fuzzy Sets and Statistical Data, *European Journal of Operational Research*, 25: 345-356.

Dubois, D., Prade, H., and Testemale, C. (1988). Weighted Fuzzy Pattern Matching, *Fuzzy Sets and Systems*, 28 (3): 313-331.

Efstathiou, J., and Rajkovic, V. (1979). Multiple Attribute Decision-Making Using a Fuzzy Heuristics Approach, *IEEE Transactions on System, Man and Cybernatics*, 9: 326-333.

Efstathiou, J., and Tong, R. (1980). Ranking Fuzzy Sets: A Decision Theoretic Approach, *IEEE Transactions on System, Man and Cybernatics*, 6: 698-703.

Eisler, R., Zaroogian, G. E., and Hennekey, R. J. 1972. Cadmium Uptake by Marine Organisms, *Journal of Fisheries Research Board of Canada*, 29: 1367-1369.

Ferson, S., 1996. What Monte Carlo Methods Cannot Do?, *Human and Ecological Risk Assessment*, 2: 990-1007.

French, D. P., and French III, F. W. (1989). The Biological Effects Components of the Natural Resource Damage Assessment Model System, *Oil and Chemical Pollution*, 5: 125 -163.

Guynnet, D., G., Come, B., Perrochet, P., and Parriaux, A. (2000). Comparing Two Methods for Uncertainty in Risk Assessments, *Journal of Environmental Engineering*, ASCE, 125 (7): 660-666.

Hall, J. (2000). Ester Based Drilling Fluids: Still the Best Environmental Option?, *Offshore* (Tulsa, Okla) 59 (9): 129-30+.

Hammonds, J. S., Hoffman, F. O. and Bartell, S. M. (1994). *An Introductory Guide to Uncertainty Analysis in Environmental Health and Risk Assessment*, SENES Oak Ridge, Inc., Oak Ridge, TN, April.

Hannah, C. G., Xu, Z., Shen, Y. and Loder, J. W. (1997). Models for Suspended Sediment Dispersion and Drift, *Proceedings of the Conference American Society of Civil Engineers*, Alexandria, Virginia.

Harrison, S. E., and Klaverkamp, J. F. (1989). Uptake, Elimination and Tissue distribution of Dietary and Aqueous Cadmium by Rainbow Trout (*salmo gairdneri* richardson) and Lake Whitefish (*coregonus clupeaformis*), *Environmental Toxicology and Chemistry*, 8: 87-97.

Hattis, D. B., and Burmaster, D. E. (1994). Assessment of Variability and Uncertainty Distributions for Practical Risk Assessments, *Risk Analysis*, 14 (5): 713-730.

Holcombe, G. W., Benoit, D. A., Leonard, E. N., and McKim, J. M. (1976). Long-term Effects of Lead Exposure of Three Generations of Brook Trout (*salvenius fontinalis*), *Journal of Fisheries Research Board of Canada*, 33: 1731-1741.

Howard, P. H. (1989). *Handbook of Environmental Fate and Exposure Data, for Organic Chemicals*, Volume I, Lewis Publishers.

Huang, H. (1992). *Transport Properties of Drilling Muds and Detroit River Sediments, Ph.D. Thesis*, University of California, Santa Barbara, U. S.

Husain, T., Sadiq, R., Mukhtasor, and Khan, A. A. (2001). Framework for Ecological Risk Assessment: Deterministic and Uncertainty Analyses, Book Chapter In: The *Gulf Ecosystem: Health and Sustainability*, Elsevier Publishers, pp. 199-218.

Hwang, C L., and Lin, M. J. (1987). *Group Decision-Making under Multiple Criteria*, Springer-Vaerlag, NY.

Hwang, C L., and Yoon, K. (1981). *Multiple Attribute Decision-Making - Methods and Applications, A State of the Art Survey*, Springer-Vaerlag, N.Y.

Iman, R. L. and Helton, S. C. (1988). An Investigation of Uncertainty and Sensitivity Analysis Techniques of Computer Models, *Risk Analysis*, 8 (1): 71-90.

Israeli, M., and Nelson, C. B. (1992). Distribution and Expected Time of Residence for U.S. Households, *Risk Analysis*, 12 (1): 65-72.

Jain, R. (1976). Decision-Making in the Presence of Fuzzy Variables, *IEEE Transactions on System, Man and Cybernatics*, 6: 698-703.

Jain, R. (1977). A Procedure for Multi Aspect Decision-Making using Fuzzy Sets. *International Journal of System Science*, 8: 1-7.

James, H. P., and Lee, Y. W. (1992). Selection of Design/Build Proposal Using Fuzzy-Logic System. *Journal of Environmental Engineering*, ASCE, 118 (2): 303-317.

Jooste, S. (2000). A Model to Estimate the Total Ecological Risk in the Management of Water Resources Subject to Multiple Stressors, *Water SA*, 26 (2): 159-166.

Jooste, S. (2001). A Possibilistic Approach to Diverse-Stressor Aquatic Ecological Risk Estimation, *Water SA*, 27 (3): 293-302.

Karman, C. C. and Reerink, H. G. (1998). Dynamic Assessment of the Ecological Risk Assessment of the Discharge of Produced Water from Oil and Gas Producing Platforms, *Journal of Hazardous Materials*, 61: 43-51.

Karman, C.C., Johnsen, S., Schobben, H.P.M., and Scholten, M.C.T. (1996). Ecotoxicological Risk of Produced Water Discharged from Oil Production Platforms in the Statfjord and Gullfaks Field, In *Produced Water 2: Environmental Issues and Mitigation Technologies*, Edited by M. Reed and S. Johnsen, Plennum Press, N.Y., pp. 127-134.

Kerre, E. E. (1982). *The Use of Fuzzy Set Theory in Electrocadiological Diagnosis*, M. M. Gupta and Sanchez, E. (Editors), pp. 277-282.

Khondaker, A. N. (2000). Modeling the Fate of Drilling Waste in Marine Environment - An Overview, *Computers and Geosciences*, 26 (5): 531-540.

Kolodziejczyk, W. (1986). Orlovsky's Concept of Decision-Making with Fuzzy Preference Relation - Further Results, *Fuzzy Sets and Systems*, 19 (1): 11-20.

Konemann, H. (1981). Fish Toxicity Tests with Mixtures of More than Two Chemicals: A Proposal for a Quantitative Approach and Experimental Results, *Aquatic Toxicology*, 19: 229-238.

Kranck, K., P. C. Smith and T. G., Milligan (1996). Grain Size Characteristics of Fine Grained Unflocculated Sediments I: 'One Round" Distributions., *Sedimentology*, 43: 1-8.

Kranck, K., Petticrew, E., T. G., Milligan and I. G. Droppo (1992). In Situ Particle Size Distributions Resulting from Flocculations. In: A J. Mehta, Nearshore and Estuarine Cohesive Sediment Transport, *Coastal Estuarine Studies Series*, 42, AGU, Washington, pp. 60-75.

Kumada, H. S., Kimura, S., and Yokote, M. (1980). Accumulation and Biological Effects of Cadmium in Rainbow Trout, Bulletin, *Japanese Society of Scientific Fisheries*, 46 (1): 97-103.

Kumada, H. S., Kimura, S., Yokote, M., and Matida, Y. (1973). Acute and Chronic Toxicity, Uptake and retention of Cadmium in Freshwater Organisms, *Bulletin, Freshwater Fisheries Research Laboratory* (Toyoko), 22 (2): 57-165.

Kwakernaak, H. (1979). An Algorithm for Rating Multiple Aspect Alternative Using Fuzzy Sets, *Automatica*, 15: 615-616.

Laarhoven, P. M. J., and Pedrycz, W. (1983). A Fuzzy Set Extension of Saaty's Priority Theory, *Fuzzy Sets and Systems*, 11 (3): 229-241.

LaGrega, M. D., Buckingham, P. L., Evans, J. C. and ERM Group (1994). *Hazardous Waste Management*, McGraw-Hill series.

Lee, E. S., and Li, R. L. (1988). Comparison of Fuzzy Numbers Based on the Probability Measures of Fuzzy Events, *Computer and Mathematics with Applications*, 15: 887-896.

Lee, W.Y. and Nichol, J.A.C. (1978). Individual and Combined Toxicity of Some Petroleum Aromatics to the Marine Amphipod *elasmopus pecpenicrus*, *Marine Biology*, 48: 215-222.

Lee, Y. W. (1992). *Risk Assessment and Risk Management for Nitrate Contaminated Groundwater Supplies, Ph.D. Dissertation*, Department of Civil Engineering, University of Nebraska, Lincoln, Nebraska.

Lee, Y. W., Bogardi, I. and Stansbury, J. (1991). Fuzzy Decision-Making in Dredged Material Management, *Journal of Environmental Engineering*, ASCE, 117 (5): 614-630.

Lenwood, W. H. Jr., Scott, M. C. and Killen, W. D. (1998). Ecological Risk Assessment of Copper and Cadmium in Surface Waters of Chesapeake Bay Watershed, *Environmental Toxicology and Chemistry*, 17 (6): 1172-1189.

Ling, H., Diamond, M., and Mackay, D. (1993). Application of the QWASI Fugacity/Aquivalence Model to Assessing Sources and Fate of Contaminants in Hamilton Harbor, *Journal of Great Lakes Research*, 19: 582-602.

Lu, RS, and Hu, JY. (1999). Analysis of Reservoir Water Quality using Fuzzy Synthetic Evaluation, *Stochastic Environmental Research and Risk Assessment*, 13: 327-336.

Lyman, W. J., Reehl, W. F. and Rosenblatt, D. H. (1990). *Handbook of Chemical Property Estimation Methods*, American Chemical Society, Washington, D. C., U.S.

Mabuchi, S. (1988). An Approach to the Comparison of Fuzzy Subsets with an α-cut Dependent Index, IEEE Transactions, *Systems, Man and Cybernatics*, 18 (2): 264-272.

Mackay, D. (1991). *Multimedia Environmental Models: The Fugacity Approach*, Lewis Publishers, Chelsea, MI.

Mackay, D. and Diamond, M. (1989). Application of the QWASI (Quantitative Water Air Sediment Interaction) Fugacity Model to the Dynamics of Organic and Inorganic Chemicals in Lakes, *Chemosphere*, 18: 1343-1365.

Mackay, D. and Paterson, S. (1990). Fugacity Models, In: *Practical Applications of Quantitative Structure-Activity Relationships (QSAR) in Environmental Chemistry and Toxicology*, Karcher, W. and Devillers, J. (Eds.), Kluwer Academic Publishers, Dordrecht, pp. 433-460.

Mackay, D., Joy, M. and Paterson, S. (1983). A Quantitative Water, Air, Sediment Interaction (QWASI) Fugacity Model for Describing the Fate of Chemicals in Lakes, *Chemosphere*, 12: 277-291.

Mackay, D., Paterson, S. and Shiu, W. Y. (1992). Generic Models for Evaluating the Regional Fate of Chemicals, *Chemosphere*, 24: 695-717.

Mackay, D., Sang, S., Vlahos, P., Gobas, F., Diamond, M. and Dolan, D. (1994). A Rate Constant Model of Chemical Dynamics in Lake Ecosystem: PCBs in Lake Ontario, *Journal of Great Lakes Research*, 20 (4): 625-642.

Maxwell, R.M. and Kastenberg, W.E.. (1999). Stochastic Environmental Risk Analysis: An Integrated Methodology for Predicting Cancer Risk from Contaminated Groundwater, *Stochastic Environmental Research and Risk Assessment*, 13 (1-2): 27-47.

McCahone, C. (1987). *Fuzzy Set Theory Applied to Production and Inventory Control, Ph.D. Dissertation*, Department of Industrial Engineering, Kansas State University.

McCarty, LS and Mackay, D. (1993). Enhancing Ecotoxicological Modeling and Assessment: Body Residues and Modes of Toxic Action, *Environmental Science and Technology*, 27: 1719-1728.

Meinhold, A. F. (1998). *Framework for a Comprehensive Environmental Assessment of Drilling Fluids*, National Petroleum Technology Office, Office of Fossil Energy, U.S. Department of Energy, Tulsa, Oklahoma, BNL-66108.

Meinhold, A. F., Holtzman, S., and Dephillips, M. P. (1996). Risk Assessment from Produced Water Discharges to Open Bays in Louisiana, In *Produced Water 2: Environmental Issues and Mitigation Technologies*, Edited by M. Reed and S. Johnsen, Plennum Press, N.Y., pp. 395-409.

Meinhold, A. F., Holtzman, S., and Hamilton, L. D. (1995). Human Health Risk Assessment for Radium Discharged Offshore in Produced Water, *Proceedings of the SPE/EPA Exploration and Production Environmental Conference*, Houston, TX.

Miller, G. A. (1965). The Magic Number Seven, Plus or Minus Seven, *Psychological Review*, 63: 81-97.

Minitab (1998), *Mintab for Windows*, Version 12.1, Mintab Inc.

MMS (1989). *Gulf of Mexico Physical Oceanography Program Final Report*: Year 5; Volume: Technical Report. USDOI, MMS, Gulf of Mexico OCS Region. OCS Study MMS 88-0067.

Moran, J. M., and Shapiro, H. N. (1988). *Fundamentals of Engineering Thermodynamics*, John Wiley & Sons, Inc. N.Y.

Morgan, M. G., and Henrion, M. (1990). *Uncertainty: A Guide to Dealing with Uncertainty in Quantitative Risk and Policy Analysis*, Cambridge University Press. 332 pp.

Mukhtasor, Sadiq, R., Husain, T., Veitch, B., and Bose, N. (2001). Acute Ecological Risk Associated with Soot Deposition: A Persian Gulf Case Study, *Journal of Ocean Engineering*, 28: 1295-1308.

Murakami, S., Maeda, S., and Imamura, S. (1983). Fuzzy Decision Analysis on the Development of Centralised Regional Energy Control System, *IFAC Symposium on Information, Knowledge Representation and Decision Analysis*, pp. 363-368.

Nakamura, K. (1982). Preference Relation on a Set of Fuzzy Utilities as a Basis for Decision Making, *Fuzzy Sets and Systems*, 20 (2): 147-162.

Neff, J.R. (1979). *Polycyclic Aromatic Hydrocarbon in the Aquatic Environment: Sources, Fates and Biological Effects*, Applied Science Publishers, London, 262 pp.

Negi, D. S. (1989). Fuzzy Analysis and Optimisation, *Ph.D., Thesis*, Department of Industrial Engineering, Kansas State University.

Pai, T. Y., Ouyang, C. F., and Leu, H. G. (2000). Oxygen Transfer in Gravity Flow Sewers, *Water Science and Technology*, 42 (3-4): 471-422.

Palisade (1997). @RISK, Risk Analysis and Simulation Ad-In for Microsoft Excel, *User's Guide*, Palisade Corporation. N.Y. U.S. 14867.

Pentreath, J. R. (1973). The Accumulation and Retention of ^{65}Zn and ^{54}Mn by the Plaice, *Pleuronectes platessa* L., *Journal of Experimental Marine Biology and Ecology*, 12: 1-8.

Proteus (2001). *Pollution Risk Offshore Technical EvalUation System*. http://www.bmtmis.com/Products/Proteus/proteus_main_page.htm.

Rabke, S. and Candler, J. (1998). Development of Acute Benthic Toxicity for Monitoring Synthetic-Based Muds Discharged Offshore, *IBC Conference on Minimising the Environmental Effects of Offshore Drilling*, Houston, Texas.

Reish, D.J., Geesey, G.G., Kauwling, T.J., Wilkes, F.G., Mearns, A.J., Oshida, P.S. and Rossi, S.S. (1980). Marine and Estuarine Pollution, *Journal of Water Pollution Control Federation*, 52: 1533-1575.

Reish, D.J., Geesey, G.G., Oshida, P.S., Wilkes, F.G., Mearns, A.J., Rossi, S.S. and Ginn, T.C. (1981). Marine and Estuarine Pollution, *Journal of Water Pollution Control Federation*, 53: 925-949.

Reish, D.J., Geesey, G.G., Wilkes, F.G., Oshida, P.S., Mearns, A.J., Rossi, S.S. and Ginn, T.C. (1982). Marine and Estuarine Pollution, *Journal of Water Pollution Control Federation*, 54: 786-812.

Reish, D.J., Kauwling, T.J. and Mearns, A.J. (1976). Marine and Estuarine Pollution, Journal of Water Pollution Control Federation, 48: 1439-1459.

Reish, D.J., Kauwling, T.J., Mearns, A.J., Oshida, P.S. and Rossi, S.S. (1977). Marine and Estuarine Pollution, *Journal of Water Pollution Control Federation*, 49: 1316-1340.

Reish, D.J., Kauwling, T.J., Mearns, A.J., Oshida, P.S., Rossi, S.S., Wilkes, F.G. and Ray, M.J. (1978). Marine and Estuarine Pollution, *Journal of Water Pollution Control Federation*, 50: 1424-1468.

Reish, D.J., Rossi, S.S., Mearns, A.J., Oshida, P.S., Wilkes, F.G. (1979). Marine and Estuarine Pollution, *Journal of Water Pollution Control Federation*, 51: 1477-1517.

Rice, S.D., Short, J.W. and Karinen, J.F. (1977). Comparative Oil Toxicity and Comparative Animal Sensitivity, In: D.A. Wolfe (Editor), *Fate and Effects of Petroleum Hydrocarbons in Marine Ecosystems and Organisms*, Pergamon Press, Elmsford, New York, pp. 78-94.

Risk Calc. (1995). *Risk Assessment with Uncertain Numbers*, Version 3.0, RAMAS, Ecological and Environmental Software.

Saaty, T. L. (1977). A Scaling Method for Priorities in Hierarchical Structures, *Journal of Mathematical Psychology*, 15: 234-281.

Saaty, T. L. (1988). *Multicriteria Decision-Making: The Analytic Hierarchy Process*, University of Pittsburgh, Pittsburgh, Pa.

Sadiq, R. (1997). *Performance Evaluation of Slow Sand Filters: A Probabilistic Approach, MS Thesis*. King Fahd University of Petroleum and Minerals. Dhahran, Saudi Arabia.

Sadiq, R. (2000). Ocean Environmental Risk Assessment of the Disposal of Drilling Muds and Rock Cuttings - A Conceptual Model. In: *The Canadian Society of Civil Engineering*, 2000 Conference London, Ontario. 7-10 June 2000.

Sadiq, R., Husain, T., Veitch, B., and Bose, N. (2001a). Marine Water Quality Assessment of Synthetic-Based Drilling Waste Discharges (Submitted to *Journal of Air, Water, and Soil Pollution*).

Sadiq, R., Husain, T., Veitch, B., and Bose, N. (2001b). Fate of Drilling Wastes in the Marine Environment: Water-Sediment Interaction Modeling. In: *Petrotech 2001*, Bahrain, October 29-31 2001.

Sadiq, R., Husain, T., Veitch, B., and Bose, N. (2001c). Heavy Metals Distribution in the Water Column and Pore Water: A Drilling Waste Case Study. In: *The Canadian Society of Civil Engineering*, Victoria, May-June 2001.

Sadiq, R., Husain, T., Bose, N. and Veitch, B. (2001d). Distribution of Arsenic and Copper in Sediment Pore Water: An Ecological Risk Assessment Case Study for Offshore Drilling Waste Discharges (Submitted to *Risk Analysis*).

Sadiq R., Kar S. and Husain T. (2001e). Chloroform Associated Health Risk Assessment using Bootstrapping: A Case Study for Limited Drinking Water Samples, *Journal of Air, Water, and Soil Pollution* (In press).

Sadiq, R., Husain, T., Bose, N., Veitch, B., and Munawar, M. (2001f). Toxaphene Distribution in the Lake Superior Trout and Associated Sublethal Ecological Risk. (Submitted to *Journal of Aquatic Ecosystem Health and Management*).

Sadiq, R., Veitch, B., Husain, T. and Bose, N. (2000). Synthetic-Based Drilling Fluids Discharge in the Marine Environment: Water Quality Assessment, *Third Speciality Conference on Environmental Progress in the Petroleum and Petrochemical Industries*, 1-3 May, Bahrain.

Saiki, M. K., Castleberry, D. T., May, T. W., Martin, B. A. and Bullard, F. N. (1995). Copper, Cadmium and Zinc Concentrations in Aquatic Food Chains from the Upper Sacramento River (California) and Selected Tributaries, *Archives in Environmental Contamination and Toxicology*, 29: 484-491.

Schaanning, M. T. (1995). *Evaluation of Overall Marine Impact of the Novadril Mud System*, NIVA Report 0-95018.

Seaconsult Marine Research Limited (2000). *Modeled Predictions of Well Cuttings Deposition and Produced Water Dispersion of the Proposed White Rose Development*. Husky Oil Operations Limited.

Siskos, J. L., Lochard, J., and Lambard, J. (1984). A Multi Criteria Decision-Making Methodology under Fuzziness: Application to the Evaluation of Radiological Protection in Nuclear Power Plants, In: *TIMS/Studies in the Management Sciences*, Vol. 20, H. J. Zimmermann (Editors), Elsevier Science Publishers, North Holland, pp. 261-283.

Sleath, J. F. A. (1984). *Seabed Mechanics*, Cambridge University, John Wiley and Sons.

Smith, J., and May, S. J. (1991). *Ula Wellsite 7/12-9 Environmental Survey 1991*. A Report to SINTEF SI from the Field Studies Council Research Centre.

Snarski, V. M., and Olson, G. F. (1982). Chronic Toxicity and Bioaccumulation of Mercuric Chloride in Fathead Minnow (*Pimephales promelas*). *Aquatic Toxicology*, 2: 143-156.

Solomon, KR, Baker DB, Richard, RP, Dixon, KR, SJ, La point, TW, Kendall, RJ, Weisskopf, CP, Giddings, JM, Geisy, JP, Hall, LW, Williams, WM. (1996). Ecological Risk Assessment of Atrazine in North American Surface Waters, *Environmental Toxicology and Chemistry*, 15 (1): 31-76.

Spehar, R. L. (1976). *Cadmium and Zinc Toxicity to Jordenella floridae*. U.S. EPA, EPA-00-3-76-096, Environmental Research Laboratory-Duluth, Office of Research and Development, Duluth, Minnesota.

Sprauge, J. B. (1969). Measurement of Pollutant Toxicity to Fish, Bioassay Methods for Acute Toxicity, *Water Research*, 3: 793-821.

Standard Methods (1998), *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, AWWA, APHA, and WEF.

Stansbury, J. S. (1991). *Risk-Cost Analysis under Uncertainty for Dredged Material Disposal, Ph.D. Dissertation*, Interdepartmental Area of Engineering, University of Nebraska, Lincoln, Nebraska.

Stansbury, J., Bogardi, Kelly W. E. (1989). Risk-Cost, Analysis for Management of Dredge Material, In: Risk-Based Decision-Making in Water Resources, *Proceedings of the 4th Conference Sponsored by the Engineering Foundation*, American Society of Civil Engineers.

Statistics Canada (2001). http://www.statcan.ca/english/Pgdb/People/Health/health26.htm.

Suter II, G. W. (1993). *Ecological Risk Assessment*, Lewis Publishers.

Sutter II, G. W. (1996). Risk Characterization for Ecological Risk Assessment of Contaminated Sites, *U. S. DOE, ES/ER/TM-200.*

Terra Nova (1996). *Development Application Terra Nova Development*, Environmental Impact Assessment, Petro-Canada.

Terra Nova (2000). *Material Safety Data Sheet* (MSDS), Petro-Canada.

Thatcher, M., Henriquez, L. R., and Karman, C. C. (1999). CHARM, An User Guide for the Evaluation of Chemicals Used and Discharged Offshore, Version 1.1, *A CIN Revised CHARM Report III.*

Thiobodeaux, L. J., Reible, D. D., and Fang, C. S. (1986). Transport of Chemical Contaminants in the Marine Environment Originating from Offshore Drilling Bottom Deposits- A Vignette Model, In: *Pollutants in Multimedia Environment*, Plenum Press, pp. 49-64.

Thompson, S. E., Burton, C. A., Quinn, D. L. and Ng, Y. C. (1972). Concentration Factors of Chemical Elements in Edible Aquatic Organisms. *UCRL-50564 Rev.* Lawrence Livermore Laboratory, University of California.

Timothy, J. I., and David, F. L. (2000). The Role of Food Web Models in the Environment Management of Bioaccumulative Chemicals, *Soil and Sediment Contamination*, 9 (3): 181-195.

Tong, R. M., and Bonissone, P. P. (1984). Linguistic Solutions to Fuzzy Decision Problems, In: *TIMS/Studies in the Management Sciences*, Vol. 20, Zimmermann, H. J. (Editor), Elsevier Science Publishers B. V., North-Holland, pp. 323-334.

Torno, H. C., Hartman L., Bogardi, I., Verhoog, F. H., and Higler, L. W. G. (1988). *Training Manual for the Environmental Evaluation of Water Resources Management and Development*, U. N. Educational, Scientific, and Cultural Organisation, Paris, France.

Tsukamoto, Y., Nikiforuk, P. N., Gupta, M. M. (1983). On the Comparison of Fuzzy Sets Using Fuzzy Chopping, In: *Control Science and Technology for Progress of Society*, H. Akashi (Editor), Pergamon Press, New York, pp. 46-51.

U.S. DOE (1998). Guidance for Treatment of Variability and Uncertainty in Ecological Risk Assessments of Contaminated Sites, U.S. Department of Energy, BJC/OR-55.

U.S. DOE (1999). *Procedure for Addressing Uncertainty and Variability in Exposure to Characterize Potential Health Risk from Trichloroethylene Contaminated Groundwater at Beale Air Force Base in California*, Daniels, D. I., Bogen, K. T. and Hall, L. C., U.S. Department of Energy, UCRL-ID-135784 Rev. 1.

U.S. EPA (1976). *Quality Criteria for Water*. U.S. Environmental Protection Agency, Washington D. C., 256 pp.

U.S. EPA (1984). *Risk Assessment and Risk Management: Framework for Decision-Making*, U.S. Environmental Protection Agency, Washington D. C., EPA 600/9-85-002.

U.S. EPA (1986a). *Guidelines for Carcinogen Risk Assessment*. U.S. Environmental Protection Agency, Washington D. C., Federal Register, 51: 33992-34003.

U.S. EPA (1986b). *Guidelines for Estimating Exposures*. U.S. Environmental Protection Agency, Washington D. C., Federal Register, 51 (185): 34042-34054.

U.S. EPA (1986c). Guidelines for Mutagenicity Risk Assessment, U.S. Environmental Protection Agency, Washington D. C., Federal Register, 51:34006-34012.

U.S. EPA (1986d). *Guidelines for the Health Assessment of Suspect Developmental Toxicants*. U.S. Environmental Protection Agency, Washington D. C., Federal Register, 51:34028-34040.

U.S. EPA (1986e). *Guidelines for the Health Risk Assessment of Chemical Mixtures*. U.S. Environmental Protection Agency, Washington D. C., Federal Register, 51:34014-34025.

U.S. EPA (1989). *Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual, Interim Final*. Office of Emergency and Remedial Response, U.S. Environmental Protection Agency, Washington D. C., EPA-540-1-89-002.

U.S. EPA (1991). *Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual, Supplemental Guidance: Standard Default Exposure Factors, Interim Final*, Office of Emergency and Remedial Response, U.S. Environmental Protection Agency, Washington D. C., OSWER Directive: 9285.6-03.

U.S. EPA (1992a). *Framework for Ecological Risk Assessment*, Risk Assessment Forum, U.S. Environmental Protection Agency, Washington D. C., EPA-630-R-92-001.

U.S. EPA (1992b). *Guidelines for Exposure Assessment*. U.S. Environmental Protection Agency, Washington D. C., EPA-600Z-92-001.

U.S. EPA (1992c). *Criteria and Related Information for Toxic Pollutants*. Water Management Division, EPA Region VI, U.S. Environmental Protection Agency, Washington D. C.

U.S. EPA (1993). *A Guidebook to Comparing Risks and Setting Environmental Priorities*, U.S. Environmental Protection Agency, Washington D. C.

U.S. EPA (1995). *Development Document for Effluent Limitations Guidelines Standards for the Coastal Subcategory of the Oil and Gas Extraction Point Source Category*. U.S. Environmental Protection Agency, Washington D. C., EPA-821-R-95-009.

U.S. EPA (1996a). *Summary Report for the Workshop on Monte Carlo Analysis*. Risk Assessment Forum. U.S. Environmental Protection Agency. Washington D.C.. EPA-630-R-96-010.

U.S. EPA (1996b). *The Metal Translator: Guidance for Calculating a Total Recoverable Permit Limit From a Dissolved Criterion*, U.S. Environmental Protection Agency. Washington D.C., EPA-823-B-96-007.

U.S. EPA (1997). *Exposure Factor Handbook, Intake of Fish and Shellfish*, Volume II, Food Ingestion Factors, U.S. Environmental Protection Agency, Washington D. C.

U.S. EPA (1998). *Guidelines for Ecological Risk Assessment. Risk Assessment Forum*. U.S. Environmental Protection Agency, Washington D. C., EPA-630-R-98-002F.

U.S. EPA (1999a). *Development Document for Proposed Effluent Limitations Guidelines and Standards for Synthetic-Based Drilling Fluids and other Non-Aqueous Drilling Fluids in the Oil and Gas Extraction Point Source Category*, U.S. Environmental Protection Agency, Washington D. C., EPA-821-B-98-021.

U.S. EPA (1999b). *Environmental Assessment of Proposed Effluent Limitations Guidelines and Standards for Synthetic-Based Drilling Fluids and other Non-Aqueous Drilling Fluids in the Oil and Gas Extraction Point Source Category*, U.S. Environmental Protection Agency, Washington D. C., EPA-821-B-98-019.

U.S. EPA (1999c). *Partition Coefficients for Metals in Surface Water, Soil, and Waste*, U.S. Environmental Protection Agency, Washington D. C., Contract No. 68-C6-0020.

U.S. EPA (1999d). *Media-to-Receptor Bioconcentration Factors (BCFs), Screening Level Ecological Risk Assessment Protocol*, Multimedia Planning and Permitting Division Center for Combustion Science and Engineering, U.S. Environmental Protection Agency, Washington D. C.

U.S. EPA (2000a). *Development Document for Final Effluent Limitations Guidelines and Standards for Synthetic-Based Drilling Fluids and other Non-Aqueous Drilling Fluids in the Oil and Gas Extraction Point Source Category*, U.S. Environmental Protection Agency, Washington D. C., EPA-821-00-013.

U.S. EPA (2000b). *Environmental Assessment of Final Effluent Limitations Guidelines and Standards for Synthetic-Based Drilling Fluids and other Non-Aqueous Drilling Fluids in the Oil and Gas Extraction Point Source Category*, U.S. Environmental Protection Agency, Washington D. C., EPA-821-00-014.

U.S. EPA (2001). *Integrated Risk Information (IRIS)*. Online Database at http://www.epa.gov./ngispgm3/iris.

Vik, E. A., Nesgard, B. S., Berg, J. D., Dempsey, S. M., Johnson, D. R., Gawel, L., and Dalland, E. (1996). Factors Effecting Methods for Biodegradation Testing for Drilling Fluids Marine Discharge, *SPE 35981*: 697-711.

Watson, S. R., Weiss, J. J., and Donnell, M. L. (1979). Fuzzy Decision Analysis. *IEEE Transactions on System, Man and Cybernatics*, 9: 1-9.

Williams, D. R., and Giesy, J. P. Jr., (1979). Relative Importance of Food and Water Sources to Cadmium Uptake by *gambusia affinis* (Poecilidae), *Environmental Research*, 16: 326-332.

Yager, R. R. (1978). Ranking Fuzzy Subsets over the Unit Interval, *Proceedings 1978, CDC*, pp. 135-1437.

Yager, R. R. (1980a). On a General Class of Fuzzy Connectives, *Fuzzy Sets and Systems*, 4: 235-242.

Yager, R. R. (1980b). On Choosing Between Fuzzy Subsets, *Kybernetes*, 9: 151-154.

Yager, R. R. (1981). A Procedure for Ordering Fuzzy Subsets of the Unit Interval, Information Sciences, 24: 143-161.

Zadeh, L. A (1965), Fuzzy Sets, *Information and Control*, 8 (3): 338-353.

APPENDIX

A1

Bootstrapping Macro

```
GMACRO
rehan.mac
do k1=1:1000
sample 32 c1 c2;
replace.
let c3=log(c2)
let c4(k1)=mean(c3)
let c5(k1)=stdev(c3)
let c6(k1)=exp(c4(k1)-1.2815 * c5(k1))
enddo
let c7=mean(c6)
let c8=stdev(c6)
endmacro
```