

Probabilistic methods used in environmental risk evaluation for groundwater protection

Pengxin Zhang

Dissertation for Ph.D. degree



Faculty of Mathematics and natural Sciences

Department of Geosciences

University of Oslo

March 2010

© Pengxin Zhang, 2010

*Series of dissertations submitted to the
Faculty of Mathematics and Natural Sciences, University of Oslo
No. 933*

ISSN 1501-7710

All rights reserved. No part of this publication may be
reproduced or transmitted, in any form or by any means, without permission.

Cover: Inger Sandved Anfinsen.
Printed in Norway: AiT e-dit AS.

Produced in co-operation with Unipub.
The thesis is produced by Unipub merely in connection with the
thesis defence. Kindly direct all inquiries regarding the thesis to the copyright
holder or the unit which grants the doctorate.

Acknowledgements

As I finish this thesis, a lot of memories come to mind. During the unforgettable days and nights of my Ph.D. study, a large number of people have been involved, and I am grateful all of them for the help and support they have given to me.

First of all, I would like to express my great gratitude to my supervisor Prof. Per Aagaard. Thank you for giving me the opportunity to pursue a Ph.D. degree. It was you who had the patience to guide me through the most difficult starting stage of the study, and offered generous help and support when I needed it; you also had great patience when revising my papers. Also my supervisor Prof. Lars Gottschalk should be gratefully acknowledged for always having given timely replies and wise advice which raised the level of my research.

My sincere thanks go to the employees of the Department of Geosciences at the University of Oslo, especially Prof. Chongyu Xu and Prof. Lena Merete Tallaksen. I would like to thank other colleague in our section. I will remember your helps, the happy lunch times we shared and your stories. Many thanks to Prof. Farrokh Nadim and Prof. Gijs Breedveld, and cooperators Ketil Haastad and Amy Dale. Thank you all for your selfless support and pleasant co-operation.

I especially want to thank my Master, Thupten Thinley Rinpoche and Jueguang, for giving me confidence and motivation during a difficult period of my life, I am very grateful for all you did for me.

I am very thankful also to my friends, Nora Jennifer Schneevoigt, Fang Yao, Haiying Liu, Kim Anh Thi Vo, Zhong Wang, Zhihong Li, Tsering Penpa, Cosmo Ngongondo, Said Suleiman Bakari and Weibiao Wang, for giving me happiness and good times that helped me through the tough times. It is you who give me courage in life, and I will never forget you. I would like also to thank other friends, whose names I will not mention here, or perhaps I don't even know your names - thank you for the help you gave me, I will remember everything you did for me, especially your smiling faces which put me in a happy mood.

Most of all I am grateful to my husband, Yibin Wang; my son, Yinhuan Wang; my parents and parents in law. Thank you all for the selfless support during these years. You deserve my love forever.

At last but not least, my sincerely thanks go to the Norwegian State Education Loan Fund for financial support these years.



Pengxin Zhang

December 2009, Oslo, Norway

Contents

Acknowledgements	I
1 Introduction.....	1
2 Environmental impact assessments and environmental risk assessment.....	5
3 Probability methods in environmental risk assessment.....	12
3.1 Description of probabilistic approach	
3.2 Monte Carlo simulation	
3.3 First- and Second- Order Reliability Method (FORM) (FORM/SORM)	
3.4 Probability methods in groundwater contamination	
4 Mass transport in saturated media	20
4.1 Darcy's law and advective transport	
4.2 Partition – Sorption relationship	
4.3 Adsorption/Retardation	
4.4 Diffusion	
4.5 Dispersion	
4.6 Biodegradation	
4.7 Contaminant transport in groundwater	
5 Flow in the unsaturated zone	27
5.1 Water content in soil	
5.2 Retention of water in soil	
5.3 Unsaturated hydraulic conductivity	
5.4 Soil water potential	
5.5 Contaminant transport in unsaturated zone	

6	Contaminant in soil	31
	6.1 Soil and contaminants	
	6.2 Oil leakage and migration	
	6.3 Contaminant transport in porous medium	
	6.4 Contaminants under study	
	• Pesticides	
	• Toluene	
	• Propylene glycol (PG)	
7	Results	38
	• Paper 1	
	• Paper 2	
	• Paper 3	
	• Conclusions and future perspectives	
8	Conclusions and future perspectives	51
9	References	53

Appendix

Paper 1-3

Conference extended abstract

Conference post and abstract

1 Introduction

Groundwater contamination issues have increasingly attracted people's attention. In the broadest sense, groundwater refers to all subsurface water. Generally, it refers to water beneath the surface of the earth which saturates the pores and fractures in sand, gravel, and rock formations.

Groundwater is a major source of water for agriculture and industry, and is an important source of drinking water for many people around the world. About 23,400,000 cubic kilometers (km³) of groundwater exist on the earth. It is estimated that approximately 46 % of the groundwater is fresh water, which accounts for about 30% of freshwater on Earth (Lipton 1996). In Europe, about 75% of EU inhabitants depend on groundwater for their water supply (EUROPA 2009). In the United States, about half of the population relies to some extent on groundwater as a source of drinking water. Groundwater is also an important resource for industry and agriculture. For instance, about 65% of agricultural irrigation in the U.S. uses groundwater. In addition, groundwater is also an important part of the water cycle; it is a major contributor to flow in many streams and rivers and has a strong influence on river and wetland habitats for plants and animals. In many rivers, more than 50% of the annual flow is derived from groundwater. In low-flow periods in summer, more than 90% of the flow in some rivers may come from groundwater (EUROPA 2009). In Norway, groundwater resources have traditionally played a minor role because there are plenty of surface water resources. However, in some places, such as the Brumunddal sandstone which is located some 150 km north of Oslo, groundwater is major resource water for both consumption and agricultural use.

Groundwater moves slowly through the subsurface. The impact of anthropogenic activities may last for a relatively long time, which means that pollution that occurred some decades ago – whether from agriculture, industry or other human activities – may still be threatening

groundwater quality today and, in some cases, will continue to do so for several generations to come. It is critical that groundwater be unpolluted for those who rely on it, yet with the growth of industry, technology, and human population, the deterioration of groundwater has accelerated. In many locations groundwater has been contaminated for many decades. The sources of contamination can be categorized into the following types (Lenntech 2009):

Natural: Groundwater moving through sedimentary rocks and soils may pick up a wide range of natural compounds such as magnesium, calcium, and chlorides. Some aquifers have high natural concentration of dissolved constituents such as arsenic, boron, and selenium.

Agricultural: Pesticides, fertilizers, herbicides and animal waste are agricultural sources of groundwater contamination. It is reported that approximately 2.5 million tons of pesticides are applied worldwide each year, and less than 0.1% of that used for pest control, actually reaches its target pests. Thus, more than 99.9% of the pesticides used move into the environment, where they may contaminate soil, water, and the atmosphere, and adversely affect ecosystems and public health (FAO 2002; 1995; Thwih and Mar 2002).

Industrial: Modern economic activity requires transportation and storage of material used in manufacturing, processing, and construction. Along the way, some of this material may be lost through spillage, leakage, or improper handling.

Residential: Residential wastewater systems can be a source of many categories of contaminants, including bacteria, viruses, nitrates from human waste, and organic compounds. Improperly storing or disposing of household chemicals such as paints, synthetic detergents, solvents, oils, medicines, disinfectants, pool chemicals, pesticides, batteries, gasoline and diesel fuel can lead to groundwater contamination, too.

To clean up groundwater is more complicated and difficult than to clean up surface water. Site contamination clean-up in groundwater can consist of:

- Containing the contaminants to prevent them from migrating from their source;
- Removing the contaminants from the aquifer;
- Remediating the aquifer by either immobilizing or detoxifying the contaminants while they are still in the aquifer.

The effectiveness of clean-up depends on the geology of the aquifer, the types of contaminant, the physical and chemical properties of the contaminants, and access to the subsurface. The clean-up time varies widely, ranging from years to decades or more. The costs, which vary with clean-up aims and local geological conditions, generally expensive. For example, the treatment and removal of methyl tert-butyl ether (MTBE), a compound added to gasoline and used in the oil refining industry, requires pumping, biobarrier and other technologies. In order to establish a 500-foot biobarrier at Port Hueneme, the costs are estimated to be between \$800 and \$1,050 per linear foot for aquifers less than 30 feet below ground surface. The annual operation and maintenance costs for a 500-foot biobarrier are estimated at approximately \$75,000 (ITRC 2005).

Groundwater pollution cannot be completely prevented. However, there are a number of steps which can be taken in order to ensure that their risks are minimized and the environment is protected from potential contamination. In Europe, the European Union Directive (85/337/EEC) on Environmental Impact Assessments (known as the EIA directive) was first introduced in 1985, to require that the impact of projects on the environment be evaluated. In 2001, this issue was enlarged to include the assessment of plans and programmes by the so-called Strategic Environmental Assessment (SEA) Directive (2001/42/EC), and this is now in force. It was proposed that environmental risk assessment be a part of SEA. An environmental risk assessment is generally described as proceeding in four steps: hazard identification, dose-response assessment, exposure assessment, and risk characterization.

Environmental risk assessment is often performed in the early stage of a programme when many uncertainties exist. The deterministic method traditionally used in risk assessment faced great challenges. In the traditional deterministic estimate, variability and uncertainty are usually managed by assuming stricter criteria, so the risk is often overestimated. In addition, deterministic calculation can give an estimate of contaminant exposure, but “a point estimate cannot tell how many will actually be above reference dose, nor how high the exposure will actually be, or whether more measurements are needed, and so on.” (Öberg and Bergback 2005). The probabilistic risk assessment, however, is able to answer these questions. In this study, we focused on exposure assessment, and combine one probabilistic approach, the First Order Reliability Method (FORM), with transport equations, to predict the probability of contaminants exceeding certain critical levels, in order to provide explicit results for the decision-maker. Reasonable hypotheses of transport in the subsurface are needed for such

studies. The required simplifications used in this study are homogeneity of the aquifer, parallel flow of constant velocity, constant retardation factors, reaction rate, and dispersivities. In addition, the pollutant input must not influence the homogeneous field-flow, and molecular diffusion is neglected.

Main objectives

- The first aim of this thesis is to derive a probabilistic methodology for environmental risk assessment of groundwater pollution, by combining probabilistic approaches with transport models in the subsurface.
- This probabilistic methodology is not completely new to groundwater pollution. But, it is applied here to different case histories where different types of contaminants are involved, thereby providing insight into the potential threat to humans and environments.
- The sensitivity analysis inherent in our methodology gives the relative weights, by importance factors, of parameters influencing the failure probability. This result will help the environmental authority to find the most critical factors, that is, the ones contributing most to the risks, and thereby to take effective actions.

We carried out three studies which applied this probabilistic approach to evaluate the risk of pollution with respect to several types of chemicals. In the first study, we considered five pesticides which are persistent chemicals in nature, as a study target. Starting with soil concentrations and geological conditions, the probabilities of pesticides exceeding certain critical levels in groundwater were obtained. The distribution of importance factors was also indicated. These results can provide a good reference for the authority when considering local water usage or evaluating environmental risk.

In the second study, toluene and propylene glycol (PG), which are commonly used chemicals at airfields, were studied. When the two chemicals enter the groundwater, the probabilities of exceeding critical levels in both continuous and instantaneous contaminant leakage scenarios were predicted in different spatial and temporal contexts. Compared to the first paper, the main contribution of this paper is that the factors of biodegradation and time were considered, as well as the amount of information available about the leakage and subsurface conditions. The concept of “no information” and “part information” of leakage was proposed.

In the third study, we considered a scenario of a railway carriage containing jet fuel spilling into the earth. The risk of toluene contaminating the unsaturated and saturated zones was predicted. Multi-models were introduced to cope with complicated situations in the unsaturated zone.

2 Environmental impact assessments and environmental risk assessment

The lack of concern for the environmental consequences of large development projects has proved costly to society. In the case of oil spills into terrestrial ecosystems, soil and groundwater contamination destroys valuable resources and upsets the balance of the ecosystem. In response to limited environmental considerations in the traditional project-planning process, and also in response to the growing concern about environmental quality, environmental impact assessments of development projects was gradually introduced both in developed and developing countries.

Environmental Impact Assessment (EIA) and Strategic Environmental Assessment (SEA)

In 1969, the National Environmental Policy Act (NEPA) was enacted, and became one of the most important American environmental legislation to date. This act emphasized the role of Environmental Impact Assessment (EIA) in sustainable development. Although the scope of this legislation was (and remains) quite narrow, the need for environmental impact assessments was quickly recognized by governments and legislatures across the world. Formal EIA requirements were soon introduced in Japan (1972), Hong Kong (1972), Canada (1973), Australia (1974), the Philippines (1977), Taiwan (1979) and the People's Republic of China (1979) (Gilpin 1995).

In Europe, the original EIA directive, Directive 85/377/EEC, was implemented in 1988. It required member states to ensure that the environmental impact of projects which are likely to have significant effects on the environment be fully assessed before consent is given for development. The EIA directive has recently been the subject of further amendments by Directive 2003/35/EC. The main aim of the amendments is to “strengthen certain core elements of the EIA procedure” (Ryall 2005). The Member States were required to implement the new amendments by June 25, 2005. In Norway, the Norwegian Parliament adopted the first general legislation on EIA in 1990, as part of the Planning and Building Act.

By the end of 2002, approximately 600 Norwegian projects had been subject to EIA (Kvaerner *et al.* 2006). At present, EIA implemented the EU Directive on Environmental Impact Assessment and the requirements of the UNECE (United Nations Economic Commission for Europe) Convention, and put stronger emphasis on the participation of the public and relevant authorities in the early stages of the procedures.

EIA can be defined as: the process of “identifying, predicting, evaluating and mitigating the biophysical, social, and other relevant effects of development proposals prior to major decisions being taken and commitments being made” (Senecal *et al.* 1999). By identifying potential alternatives and adverse impacts, nations can better achieve goals for sustainable development, avoid or mitigate adverse environmental, social and cultural impacts, reduce costs, better plan for needed infrastructure and avoid loss of irreplaceable resources. Figure 2-1 illustrates the process of Environmental Impact Assessment (EIA).

The EIA process consists of three stages (MERL 2001) (**Fig.2-1**):

1. Screening: A general overview of possible environmental effects. At this stage, it should be determined if an EIA is required.
2. Scoping: The primary purpose of scoping is to identify concerns and issues which are important to project decisions. During this EIA stage, the content of the EIA report will be established, and the methods to be applied in forecasting negative impacts on the environment will be evaluated.
3. The EIA study and preparation of the EIA report. This phase of the EIA focuses on several main tasks: description of the environmental information, identification and forecasting of potential impacts, assessment of environmental impacts and mitigation measures.

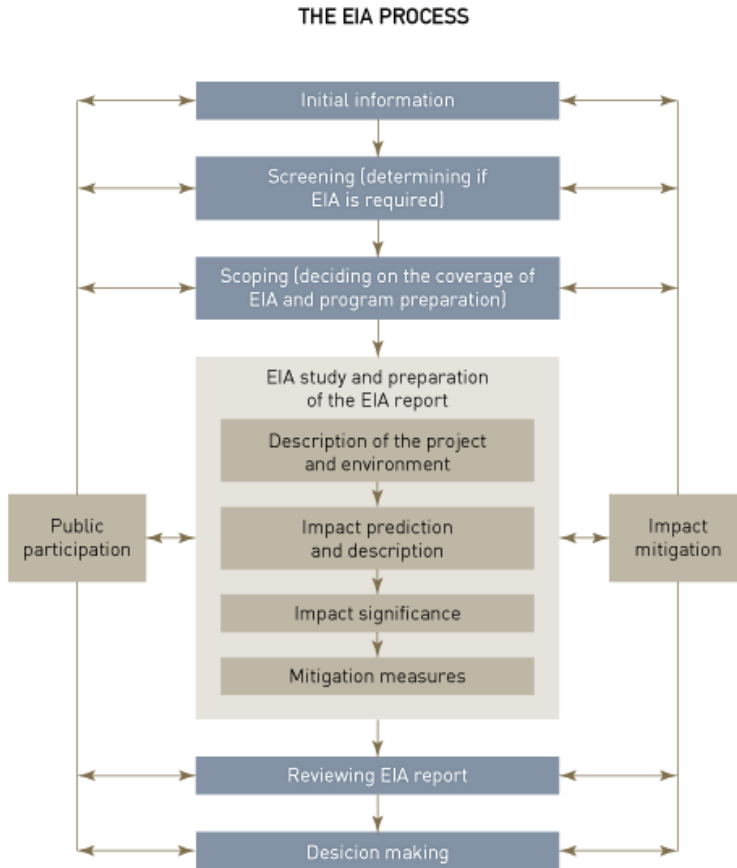


Fig. 2-1. EIA process diagram (source: Manual for Environmental Impact Assessment, Ministry of Environment of the Republic of Lithuania, Institute of Environment of Finland, 2001).

EIA has become a major tool in European environmental policy during the last 20 years. To a certain degree, EIA has prevented manifestly bad projects from receiving serious consideration. It ensures that the process of development is open to scrutiny. Alternative approaches, technologies, and sites have then been discussed. However, it is important to recognize that EIA has its limitations. Traditionally, the EIA has been concerned with individual projects, and isolated projects. It cannot cope with wider problems concerning regional economical development, social and environmental sustainable development. In addition, EIA ignores a wide range of impacts, including cumulative impacts, global impacts, indirect/secondary or induced impacts, and synergistic impacts (where impact A + impact B have a total impact

that is greater than A + B) (Alshuwaikhat 2005; Wood and Therivel 2006). Furthermore, EIA cannot be regarded as a mean of introducing an environmental “veto” power into the administrative decision-making processes. Decisions that are unsatisfactory from an environmental point of view can still be made, but with a fuller knowledge of the environmental consequences (Perneczky 2008). According to the current EIA (Directive 2003/35/EC), practice “does not appear to pay sufficient attention to ‘risk’ and ‘health impacts’; has inadequate mechanisms for ensuring ‘access to justice’; and has a dearth of formal measures for facilitating control of the quality of EIA procedures” (Ryall 2005). Strategic Environmental Assessment (SEA) is designed to fill this gap by requiring assessment of public plans and programmes. Directive 2001/42/EC (SEA Directive) is therefore supposed to be an important step forward in European environmental law (Perneczky 2008).

SEA is the process by which environmental considerations are required to be fully integrated into the preparation and adoption of plans and programmes. The objective of the SEA process is to provide for “a high level of protection of the environment and to contribute to the integration of environmental considerations into the preparation and adoption of specified plans and programmes with a view to promoting sustainable development” (2004). Although the terms of SEA vary between countries, Directive 2001/42/EC on the assessment of certain plans and programmes on the environment requires Member States to ensure environmental assessment procedures at the plan-making stage (Risse *et al.* 2003). It applies to national, regional and local plans prepared by competent authorities which are likely to have significant effects on the environment. Assessment is to be required for “plans which are prepared for agriculture, forestry, fisheries, energy, industry, transport, waste management, water management, telecommunications, tourism, town and country planning or land use” (Risse *et al.* 2003).

SEA helps decision-makers reach a better understanding of how environmental, social and economic considerations fit together. Without that understanding, we risk turning today’s development successes into tomorrow’s environmental challenges. In short, SEA helps decision makers think through all the consequences of their actions. Table 2-1 is a comparison between SEA and EIA.

Table 2-1. SEA and EIA comparison (OECD 2006)

EIA of projects	SEA of Policies, Plans and Programmes
Applied to specific and relatively short-term (life-cycle) projects and their specifications.	Applied to policies, plans and programmes with a broad and long-term strategic perspective.
Takes place at early stage of project planning once parameters are set.	Ideally, takes place at an early stage in strategic planning
Considers limited range of project alternatives	Considers a broad range of alternative scenarios
Usually prepared and/or funded by the project proponents	Conducted independently of any specific project proponent.
Focus on obtaining project permission, and rarely with feedback to policy, plan or programme consideration.	Focus on decision policy, plan and programme implications for future lower-level decisions.
Well-defined, linear process with clear beginning and end (<i>e.g.</i> from feasibility to project approval).	Multi-stage, iterative process with feedback loops.
Preparation of an EIA document with prescribed format and contents is usually mandatory. This document provides a baseline reference for monitoring.	May not be formally documented.
Emphasis on mitigating environmental and social impacts of a specific project, but with identification of some project opportunities, offsets, etc.	Emphasis on meeting balanced environmental, social and economic objectives in policies, plans and programmes. Includes identifying macro-level development outcomes.
Limited review of cumulative impacts, often limited to phases of a specific project. Does not cover regional-scale developments or multiple projects.	Inherently incorporates consideration of cumulative impacts.

SEA is an integrated process with a broad range of alternative scenarios. For the exposure assessment which we are concerned with, *modeling* or *forecasting* of direct environmental effects and *risk analysis* or *assessment* are two important tools in strategic environmental assessment (OECD 2006). It is necessary to introduce some basic definitions here.

Hazard: A hazard is an act or phenomenon that has the potential to produce harm or other undesirable consequences to some person or thing (MMC 2002). A hazard reflects a potential threat to humans as well as the impact of an event on society and the environment. Hazards are in part socially constructed by people's perceptions and their experiences. Moreover, people contribute to, exacerbate, and modify hazards. Thus, hazards can vary by culture, gender, race, socioeconomic status, and political structure (Mitchell *et al.* 1997).

Risk: Risk is a more difficult concept to define. The term “risk” is used in everyday language to mean “the probability of harmful consequences or expected losses resulting from a given hazard to a given element at danger or peril over a specified time period” (Schneiderbauer and Ehrlich 2004).

When used in the process of risk assessment, risk has most commonly been described as being “the combination of the probability, or frequency, of occurrence of a defined hazard and the magnitude of the consequences of the occurrence” (ESPON 2003). Risk can be also defined as: a measure of the probability and severity of an adverse effect to life, health, property, or the environment. Quantitatively, $\text{Risk} = \text{Hazard} \times \text{Potential Worth of Loss}$. This can also be expressed as the “Probability of an adverse event times the consequences if the event occurs”.

Risk assessment: In broad terms risk assessments are carried out to examine the effects of an agent on humans (Health Risk Assessment) and ecosystems (Ecological Risk Assessment). Risk assessment is the use of a factual base to define the health effects of exposure of individuals or populations to hazardous materials or situations, including any or all of the following components of risk assessment: hazard identification, dose-response assessment, exposure assessment and risk characterization (EPA 1999).

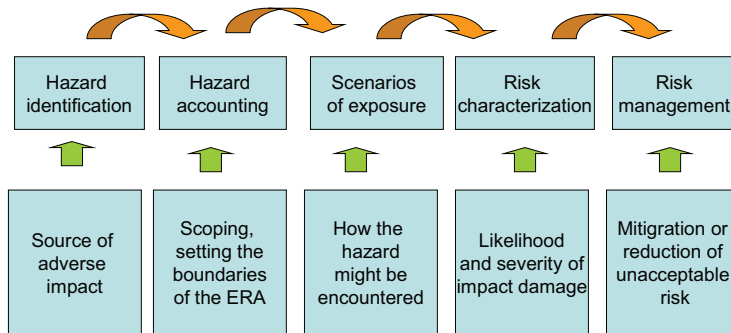
Environmental Risk Assessment (ERA): ERA is an extension of EIA, undertaken when uncertainties are large and important to project success (Bindu N.Lohani 1997). ERA, is a process of evaluating the likelihood of adverse effects in, or transmitted by, the natural environment from hazards that accompany human activities (Bindu N.Lohani 1997). It includes human health risk assessments, ecological or ecotoxicological risk assessments, and specific industrial applications of risk assessment that examine end-points in people, biota or

ecosystems (Fairman *et al.* 1998). The questions that environmental risk assessment should address are

- Whether it will lead to unpredicted adverse effects?
- How much adverse effect can be reduced/remedied?
- How to describe the magnitude or seriousness of the adverse effect?
- What is the probability of an adverse consequence?

The Asian Development bank promoted five steps in performing Environmental Risk Assessment (ADB 1997).

The five step sequence in performing ERA



Source: Asian development bank (1999)

Policy makers can use environmental risk assessment results to implement, or improve legislation, regulations or other controls to protect human health and/or the environment. If a threat to human health or the environment is identified through environmental risk prediction, risk management is performed to consider the need to impose measures to control or manage the risk.

Probabilistic Risk Assessment (PRA): PRA is a risk assessment that use probabilistic methods (e.g., Monte Carlo Analysis) to derive a distribution of risk based on multiple sets of values sampled for random variables (EPA 1999).

Probabilistic modeling: A technique that utilizes the entire range of input data to develop a probability distribution of exposure to risk rather than a single point value. The input data can be measured values and/or estimated distributions. Values for these input parameters are sampled thousands of times through a modeling or simulation process in order to develop a distribution of likely exposure or risk. Probabilistic models can be used to evaluate the impact of variability and uncertainty in the various input parameters, such as environmental exposure levels, fate and transport processes. (EPA 2009).

3 Probability methods in environmental risk assessment

Probabilistic Risk Analysis (PRA) has been used since World War II (Garrick 2002). However, the application of PRA to human health and ecological risk assessment is a more recent phenomenon.

When performing environmental risk assessment, it is in the early stage of a project/programme that there are a lot of uncertainties due to lack of knowledge, limited data, imperfect models for exposure pathways, etc. Traditional deterministic analyses meet with great challenges. In 1997, the U.S. Environmental Protection Agency (EPA) announced the “Policy for Use of Probabilistic Analysis in Risk Assessment at the U.S. EPA”, indicating the Agency's interest in using probabilistic analysis in human health and ecological risk assessment. This document states that it is “the policy of the U.S. Environmental Protection Agency that such probabilistic analysis techniques as Monte Carlo analysis, given adequate supporting data and credible assumptions, can be viable statistical tools for analyzing variability and uncertainty in risk assessments” (EPA 2000).

At the EPA, environmental risk assessments typically fall into one of two categories: human health risk assessment or ecological assessment. New guidelines and tools are continuously being developed for different areas by the EPA, such as: Draft Review of an Approach to Using Toxicogenomic Data in U.S. EPA Human Health Risk Assessments; Assessment of the Impacts of Global Change on Regional U.S. Air Quality: A Synthesis of Climate Changes Impacts on Ground – Level Ozone (NCEA/Global); Science and decisions: Advancing Risk Assessment (NAS), etc. Norway has endorsed The EU directives regarding Environmental Impact Assessment and Strategic Environmental Assessment (SEA), and the Norwegian legislation is consistent with these (Kvaerner *et al.* 2006). The Norwegian Pollution Control

Authority formulated the Guidelines for the Risk Assessment of Contaminated Sites in 1999 (SFT 1999). This guidance was developed for risk assessment of contaminated sites in relation to the use of the land. It involves a step by step approach where alternative acceptance criteria can be generated. It also presents the revised soil quality guidelines for most sensitive areas of land use.

Traditionally, risk assessment of soil and groundwater relies on deterministic analysis, suitable parameters, material properties, geography conditions are assumed. An analysis is then performed to provide a more or less detailed description of the contamination. However, when performing environmental risk assessment, it is in the early stage of a project/programme, and uncertainties in the input parameters and the models used for the assessment can be significant. These uncertainties are due to lack of knowledge, limited data, spatial variation of parameters of interest, imperfect models for exposure pathways, etc. So, the procedure for deterministic analysis of risk assessment does not address the uncertainties at all and the final result is a yes/no answer. In contrast, the strength of probabilistic methods is that they have great power for dealing with uncertainties.

3.1 Description of probabilistic approach

The probabilistic approach is the most widely used method of uncertainty analysis used in mathematical models. In the probabilistic approach, uncertainties are characterized by the *probabilities* associated with *events*. An event corresponds to any of the possible states a physical system can assume. The *probability* of an *event* can be interpreted in terms of the frequency of occurrence of that event. In the study of environmental pollution, for example, the situation where the contaminant concentration exceeds a regulatory level can be an event. There are several definitions of probability. One classical definition is given by the simple relationship (Eq. 3.1):

$$probability = \frac{Number\ of\ possible\ outcomes}{Total\ number\ of\ cases} \quad (3.1)$$

When a large number of *samples* or *events* are considered, the probability of an event is defined as the ratio of the number of times the event occurs to the total number of samples or events. A probability of 0 for an event means that the event will never occur, and a probability of 1 indicates that the event will always occur (Isukapalli 1999).

3.2 Monte Carlo simulation

Monte Carlo simulation has been introduced as a probabilistic modeling tool and illustrated in detail in many text books, such as Melchers (1999), and Madsen (1986). It is a technique that involves using random numbers and probabilities to solve problems. The Monte Carlo method is just one of many methods for analyzing uncertainty propagation, where the goal is to determine how random variation, lack of knowledge, or error affects the sensitivity, performance, or reliability of the system that is being modeled. The difference between a deterministic model and a probabilistic model can be shown by the following sketch (**Fig. 3-1**) (Wittwer 2004).

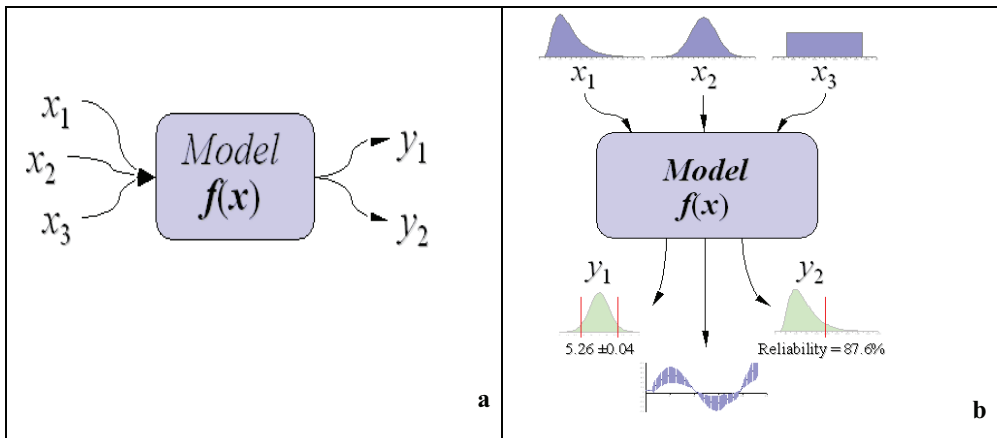


Fig. 3-1. Sketch of the difference between deterministic model and probabilistic model. Deterministic model maps a set of input variables to a set of output variables, **3-1a**. In the probabilistic model, both inputs and outputs are randomly generated from probability distributions, **3-1b** (Wittwer 2004).

Deterministic, usually means that you get the same results no matter how many times you re-calculate. Monte Carlo simulation is categorized as a sampling method because the inputs are randomly generated from probability distributions to simulate the process of sampling from an actual population. So, we try to choose a distribution for the inputs that most closely matches data we already have, or best represents our current state of knowledge. The data generated from the simulation can be represented as probability distributions (or histograms) or converted to error bars, reliability predictions, tolerance zones, or confidence intervals (**Fig.**

3-1). Five simple steps listed below shows the basic processes of probabilistic methods (Wittwer 2004):

Step 1: Create a parametric model, $y = f(x_1, x_2, \dots, x_q)$.

Step 2: Generate a set of random inputs, $x_{i1}, x_{i2}, \dots, x_{iq}$.

Step 3: Evaluate the model and store the results as y_i .

Step 4: Repeat steps 2 and 3 for $i = 1$ to n .

Step 5: Analyze the results using histograms, summary statistics, confidence intervals, etc.

3.3 First- and Second- Order Reliability Methods (FORM/SORM)

Monte Carlo simulation has been widely used in statistics, mathematics, physical sciences, finance and other areas. However, this approach proved to be costly and time consuming, especially in performing parametric and sensitivity studies since the process may have to be repeated tens or even hundreds or thousands of times in order to get an acceptable scatter in the ensemble results (Cizelj *et al.* 1994; Hamed and El-Beshry 2006; Skaggs and Barry 1997). An alternative probabilistic methodology, First-and Second Order Reliability Method (FORM /SORM), is proposed in this paper. With the FORM method, variability and uncertainty in the input parameters (variables and constants) are described by probability distributions, and the output (risk) is likewise presented as a probability of failure to exceed a critical level. A by-product of probabilistic risk assessment is a systematic sensitivity analysis of the uncertainties in the input parameters. This has proven to be a powerful tool for identifying the main sources of uncertainty and for designing efficient testing procedures. Details about the methods were described by Madsen *et al.* (1986). Considering the case of contaminant transport in groundwater, a brief introduction is as follows:

Parameters in the contaminant transport equation (for instance, **Eq 4.16**) are considered to be certain when applying a deterministic approach, while the parameters are each, more or less, uncertain in reality. In the FORM/SORM methods, parameters are considered to be random variables $\mathbf{X} = (X_1, X_2, \dots, X_n)$. A performance function is defined such that $g(\mathbf{X}) \geq 0$ means that the allowable concentration is greater than the exposure concentration (safe state), while

$g(\mathbf{X}) < 0$ means the opposite (failure state), and is linked to the tolerance concentration. These random variables are transformed using a nonlinear one-to-one mapping to the standard normal space of uncorrelated normally distributed variable, \mathbf{X} , of zero mean and unit variance. Then, the transformed limit – state surface, $g(\mathbf{X}) = 0$, is approximated at a point on the surface which is closest to the origin. This point is called the *design point*, and it is the most likely failure point in the standard normal space. The distance from the origin to the design point in the standard space is termed the *reliability index*, β , and is a measure of the reliability of the system considered. If the joint probability density function $F_x(\mathbf{X})$ is known, then the probability of failure P_f is given by

$$P_f = \int_L F_x(X) dX \quad (3.2)$$

L is the domain of \mathbf{X} , and $g(\mathbf{X}) < 0$. In general, the above integral cannot be solved analytically, and an approximation is obtained by the FORM or SORM approach.

In the FORM approach, the general case is approximated to an ideal situation where \mathbf{X} is a vector of independent Gaussian variables with zero mean and unit standard deviation, and where $g(\mathbf{X})$ is a linear function. The probability of failure P_f is then:

$$P_f = P(g(\mathbf{X}) < 0) = P\left(\sum_{i=1}^n \alpha_i X_i - \beta < 0\right) = \Phi(-\beta) \quad (3.3)$$

where $P(\dots)$ indicates “the probability that”, the vector of the direction cosines of the random variables (α_i) is called the vector of sensitivity factors, or uncertainty importance factors (Hamed 1997), β is the distance between the origin and the hyperplane $g(\mathbf{X}) = 0$, called the reliability index. n is the number of basic random variables, and Φ is the standard normal distribution function.

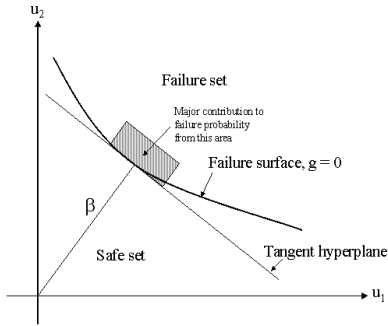


Fig. 3-2. The FORM approximations for 2 variables in the transformed U-space

The major advantage of the nonlinear mapping is the rotational symmetry of the probability density in the standard normal distances which means that for all hyperplanes of equal distance from the origin, the probability content of the half space away from the origin is constant. Furthermore, the probability density in the standard normal space decays exponentially with the square of the distance from the origin. Therefore, the primary contribution to the probability integral in Eq. 3.3 comes from the part of the failure region closest to the origin. Consequently, the design point is an optimum point at which to approximate the limit – state surface $g(\mathbf{X}) = 0$ (Hamed and Bedient 1997), using a linear (first – order) approximation in FORM and quadratic (second- order) approximation in SORM.

The most common implementation of the FORM approximation is carried out in two steps:

1. The vector of basic random variables \mathbf{X} is transformed into a vector \mathbf{U} of independent Gaussian variables with zero mean and unit standard deviation, using Rosenblatt’s transformation.
2. The (transformed) limit state function is linearized at the point of maximum probability density. This is the most likely “failure” point and is referred to as the “design point”. The design point is found by optimisation techniques.

The first-order reliability index is the shortest distance between the origin and the design point in the transformed U-space (Hasofer and N.C.Lind 1974), schematically shown in figure 3-2 for two random variables.

The performance function for the evaluation of the probability of exposure to an undesirable substance is defined as:

$$g = C_{limit} - C_{in\ situ} \quad (3.4)$$

where C_{limit} is the tolerance concentration for receptors and $C_{in\ situ}$ is the actual *in situ* concentration of the undesirable substance.

The sensitivity analysis, which is an integral part of the FORM/SORM method, provides valuable information including uncertainty importance factors (Madsen *et al.* 1986). Independent variables, such as those considered herein, are defined as the derivative of the first order reliability index with respect to the corresponding variable in the standard normal space, and this is given by

$$\left. \frac{\partial \beta}{\partial u_i} \right|_{U=U^*} = \alpha_i \quad (3.5)$$

The sum of vector of sensitivity factors (α_i) squared is equal to one, that is:

$$\sum \alpha_i^2 = 1 \quad (3.6)$$

α_i^2 , which represents the uncertainty importance factors, is applied in this study. Importance factors allow for the identification of the random variables that have the most impact on the final reliability outcome. Therefore, the importance factors are also useful for reducing the number of basic random variables in large, complex reliability models.

3.4 Probability methods in groundwater contamination

Groundwater contaminant issues have caused great attention in the past several decades, and related research has developed rapidly. With the development of the computer, probabilistic methods are now being applied in many aspects of groundwater research.

Probabilistic methods have been used to analyze and improve groundwater flow. A lot of research has been done in these areas by the traditional probabilistic method, the Monte Carlo Simulation (MCS) method (Bekesi and McConchie 1999; Binkowitz and Wartenberg 2001;

Huang *et al.* 2003; Lahkim and Garcia 1999; Liu *et al.* 2004; Marseguerra and Zio 2001; McNab 2001; Rong *et al.* 1998). MCS and First- and Second- Order Reliability Methods (FORM/SORM) methods have been applied to groundwater contamination and remediation problems (Hamed and Bedient 1997; Hamed and El-Beshry 2006; Jang *et al.* 1994; McKone and Bogen 1991). Hamed and Bedient (1997) applied the reliability methods to assess the probability of cancer risk due to ground-water contamination. Results of the reliability methods compared closely with a published case study of volatile organic chemical tetrachloroethylene (perchloroethylene PCE) contamination of a ground-water supply in California (McKone and Bogen 1991). When the FORM/SORM methods are applied to groundwater flow and solute transport equations under steady state conditions, the uncertainty boundaries obtained by the FORM/SORM methods correspond closely to the results obtained by the Monte Carlo methods (Kunstmann *et al.* 2002). When using the FORM method to analyze the transport of benzene in groundwater, Hamed and El-Beshry's (2006) results also matched those obtained by Monte Carlo simulation methods. Other examples where FORM/SORM methods were applied in groundwater problems can be found in Cawfield and Wu (1993) , Jang. *et al.* (1994), Hamed *et al.* (1995), Dimakis (1997), and Skaggs and Barry (1997).

For environmental risk assessment of groundwater, as discussed above, many uncertainties exist where probability methods are applied (Biswas 1992; Gaganis and Smith 2008; Vinten *et al.* 2009). For instance, MCS has been applied to numerous health risk assessment and contaminant probability analyses (Blanset *et al.* 2007; Ham *et al.* 2007; Macintosh *et al.* 1994; Sarang *et al.* 2008; Smith 1994). In addition, fuzzy logic has been successfully applied in some areas where conventional model based approaches are difficult or not cost effective to implement (Bogardi and Ducksteinz 2002; Kentel and Aral 2004; Kumar and Schuhmacher 2005).

Probabilistic approach has also been used in contamination research of the unsaturated zone. Using the top down probabilistic modeling approach, the contaminant transport in the unsaturated zone was described (Plimmer 1998). Utilizing the reliability theory, Boateng (1999) used three soil samples to analyze the sensitivity of the contaminant transport in two dimensions of the unsaturated zone. Apul *et al.* (2005) used the HYDRUS2D code to solve the Richards' equation and the advection-dispersion equation with retardation. By combining a geostatistical generator using the turning bands method and a multi-phase transport code

TOUGH2, Chen *et al.* (2003) successfully analyzed the impact on the environment and public health of leakage from nuclear waste storage sites. Wong (2003) used a fuzzy rule-based model to predict the contaminants' travel time to the groundwater table.

The probabilistic method used in this study is based on the deterministic contaminants transport equations in the saturated and unsaturated zones. The parameters of these equations are not known in precise detail and thus contain uncertainty. Therefore, they will be considered to be random variables, i.e. random variables $\mathbf{X} = (X_1, X_2, \dots, X_n)$ in the FORM/SORM method. When applying random variables to the deterministic transport equation, the probability of contaminants exceeding a certain critical level can be obtained.

4 Mass transport in saturated media

When chemicals are transported in the groundwater, several processes can change their mobility and concentration. They can be adsorbed onto surfaces of the mineral grains or solid organic carbon, which retards their transport compared to the velocity of water. Physical processes like diffusion and dispersion also cause concentration changes. Chemical processes such as oxidation/reduction, and degradation, especially, may also reduce their concentration. Thus, the combined effect of advection, dispersion, adsorption/desorption, volatilization, and decomposition, including biodegradation, will control migration of chemicals in underground aquifers (Freeze and Cherry 1979; Grenney *et al.* 1987; Kostecki and Calabrese 1990).

4.1 Darcy's law and advective transport

The first experimental study of groundwater flow was performed by Henry Darcy in 1856. He found that the one-dimensional flow of water through a pipe filled with sand was proportional to the cross-sectional area and the head loss along the pipe and inversely proportional to the flow length. The driving forces for the movement of soil water are described by the gradient of the hydraulic head function. Darcy's law can be expressed as

$$Q = -kA \frac{dh}{dx} \quad \text{or} \quad (4.1)$$

$$v_D = -k \frac{dh}{dx} \quad (4.2)$$

Where

- Q = Volumetric discharge
- k = Hydraulic conductivity
- A = Cross- sectional area
- v_D = Darcy velocity
- dh/dx = Gradient of hydraulic head

Buckingham (1907) first proposed that Darcy's equation is also valid for flow in unsaturated media in a modified form in which k , instead of being a constant, is regarded as a function of the volumetric water content θ (Jensen 2001). To emphasize the strong dependency of θ on the unsaturated hydraulic conductivity k and h , the pressure head, Darcy's equation in the unsaturated zone can be written as

$$v_D = -k(\theta) \frac{dh(\theta)}{dz} \quad (4.3)$$

where $dh(\theta)/dz$ is the hydraulic gradient.

The real pore water velocity v_w , responsible for advective transport

$$v_w = v_D / n_e \quad (4.4)$$

Where n_e represents effective porosity.

The transport of chemicals and other contaminants in porous geological media is mainly governed by advective transport, which is dependent on an advective flow velocity, and diffusive transport, which depends on a concentration gradient. The fundamental processes governing these basic modes of transport can be non-linear, and therefore highly dependent on the micro-structure of the porous medium (Selvadurai 2002). In environmental risk assessment, the linear theories associated with basic transport processes provide useful first approximations for the study of advective processes. The advective velocity, which is in its linear form, is used as pore water velocity, and can be solved by the advective transport equation.

4.2 Partition-Sorption relationship

The partition coefficient (K_d) – based approach is most commonly applied to hydrophobic (or “water-hating”) organic molecules as they absorb onto solid particles. Sorption of an organic pollutant to soil is a function of the soil’s organic carbon content (f_{oc}) and the chemical’s organic carbon-water partition coefficient (Karickhoff 1981; Matthes 1989; Schwarzenbach and Westall 1985).

$$K_d = K_{oc} \cdot f_{oc} \quad (4.5)$$

Where K_{oc} is the organic carbon-water partition coefficient (l/kg), f_{oc} is the fraction of organic carbon in soil, and K_d is the soil/water partition coefficient (l/ kg).

When values of K_{oc} and f_{oc} are known, the K_d value can be determined from Eq.4.5. Organic carbon content can be measured in the laboratory on porous-medium samples. $\log K_{oc}$ has a good correlation with $\log K_{ow}$, which is the octanol- water partition coefficient. Some empirical equations can estimate K_{oc} .

Karickhoff (1981):

$$\log K_{oc} = -0.21 + \log K_{ow} \quad (4.6)$$

Schwarzenbach and Westall (1985):

$$\log K_{oc} = 0.49 + 0.72 \log K_{ow} \quad (4.7)$$

SFT (1999):

$$\log K_{oc} = 1.04 \log K_{ow} - 0.84 \quad (4.8)$$

4.3 Adsorption/Retardation

When solutes dissolve in groundwater, they can be adsorbed onto the surfaces of the mineral grains of the aquifer, or absorbed by organic carbon that might be present in the aquifer. As a result of sorption processes, some solutes will move much slower through the aquifer than the groundwater that is transporting them; this effect is called retardation. Biodegradation and precipitation will decrease the concentration of a solute in the plume but may not necessarily

slow the rate of plume movement. Retardation (R) is defined simply by a mathematical expression (Eq. 4.9), assuming rapid and linear absorption and neglecting dispersion. Figure 4-1 shows a sketch of the function retardation.

$$R = 1 + \frac{\rho_d}{n_e} K_d \quad (4.9)$$

Where

- ρ_d = bulk density of aquifer
- n_e = effective porosity
- K_d = partition coefficient (L/kg).

Hence, if the average linear groundwater velocity in the x-direction is v_x , the average velocity of the solute front, v_c , is given by

$$v_c = \frac{v_x}{R} \quad (4.10)$$

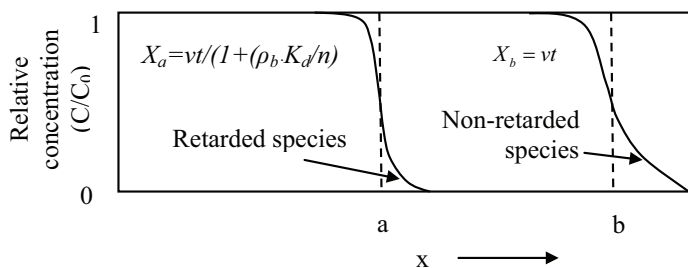


Fig.4-1. Advance of adsorbed and non-absorbed solutes through a column of porous materials. Partitioning of adsorbed species is described by K_d . Relative velocity = $1 / [1 + (\rho_b / n) K_d]$. Solute inputs are at concentration C_0 at $t > 0$ (Freeze and Cherry 1979).

4.4 Diffusion

A solute in water will move from an area of greater concentration toward an area of lesser concentration. This process is known as molecular diffusion, or simply, diffusion. Diffusion will occur as long as a concentration gradient exists, even if the fluid is not moving. Fick's first law represents the flux of chemicals to the concentration gradient:

$$F = -D_d \frac{\partial C}{\partial x} \quad (4.11)$$

Where

- F = Mass flux of solute per unit area per unit time (mol/s/m^2)
- D_d = Diffusion coefficient (m^2/s)
- C = Solute concentration (mol/m^3)
- x = Distance (m)

4.5 Dispersion

Groundwater flowing through a sand layer is forced to move around the sediment grains. The resulting spreading of a concentration front is called dispersion. On the microscopic scale, dispersion is caused by three mechanisms. The first occurs in individual pore channels. This is because water in the center of a pore space travels faster than the water near the wall. The second process is caused by diversion of flow paths around individual grains of porous material leading to variations in average velocity among different pore spaces. The third dispersive process is related to the tortuosity, branching, and inter-fingering of pore channels (Freeze and Cherry 1979).

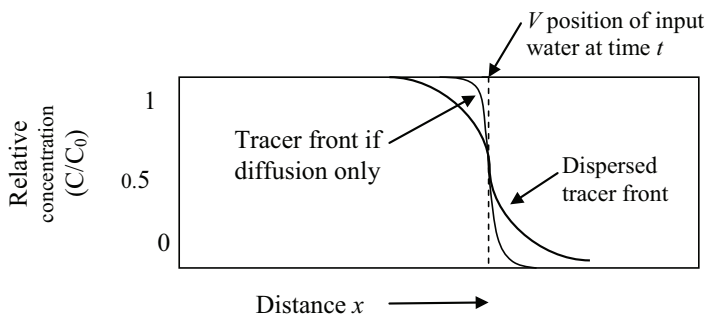


Fig. 4-3. Advective transport and the influence of longitudinal dispersion and diffusion on the transport of a solute in one-dimensional flow (Fetter 1988).

Solution of the advective transport equation yields a sharp concentration front. On the advancing side of the front, the concentration is equal to that of the invading groundwater, whereas on the other side of the front it is unchanged from the background value. This is known as plug flow, with all the pore fluid being replaced by the invading solute front. The

sharp interface that results from plug flow is shown as figure 4-3. The vertical dashed line at V represents an advancing solute front due to advection alone.

There are two types of dispersion: *longitudinal* dispersion (D_L) is caused along flow lines around grains, whereas *transverse* dispersion (D_T) is due to step over onto adjacent flow lines by diffusion (Appelo 2005). These can be represented by the following formulas (Fetter 1988):

$$D_L = \alpha_L v_i + D^* \quad (4.12)$$

$$D_T = \alpha_T v_i + D^* \quad (4.13)$$

Where

D_L = hydrodynamic dispersion coefficient parallel to the principal direction of flow (longitudinal)

D_T = hydrodynamic dispersion coefficient perpendicular to the principal direction of flow (transverse)

α_L = longitudinal dynamic dispersivity

α_T = transverse dynamic dispersivity

D^* = effective diffusion coefficient, which is related to the tortuosity.

v_i = the average linear velocity in the i direction

4.6 Biodegradation

Many organic chemicals are degraded by microbial or chemical reactions, which may depend in a complicated manner on temperature, pH, microbial population density, and other factors. The degradation process may in some cases be approximated by a simple first-order decay model, which states that the decay is proportional to the concentration:

$$\frac{\partial C}{\partial t} = -\lambda C \quad (4.14)$$

Where λ is the first-order decay constant.

4.7 Contaminant Transport in groundwater

In porous medium, advection, dispersion, diffusion, and biodegradation are the governing processes for contaminant transport (Appelo 2005). The advection-dispersion-reaction equation of contaminant transport with first order degradation rate expressed in three dimensions, takes the form (Freeze and Cherry 1979; Kinzelbach 1986):

$$\frac{\partial C}{\partial t} = \frac{D_x}{R} \frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R} \frac{\partial^2 C}{\partial y^2} + \frac{D_z}{R} \frac{\partial^2 C}{\partial z^2} - \left(v_x \frac{\partial C}{\partial x} + v_y \frac{\partial C}{\partial y} + v_z \frac{\partial C}{\partial z} \right) - \lambda C \quad (4.15)$$

As the contaminant mass is transported through the flow system, in the boundary condition as:

$$\begin{aligned} C(x, y, z, 0) &= 0 & x, y, z &\geq 0 \\ C(0, 0, 0, t) &= C_0 & t &\geq 0 \\ C(\infty, \infty, \infty, t) &= 0 & t &\geq 0 \end{aligned}$$

when considering the contaminant degradation as in first order rate, the concentration distribution of the contaminant mass at time t is given by

$$C(x, y, z, t) = \frac{M_0 R}{8(\pi t)^{3/2} V n_e \sqrt{\alpha_x \alpha_y \alpha_z v_x v_y v_z} / R} \exp \left[-\frac{(x - v_x t / R)^2}{4 \alpha_x v_x t / R} - \frac{(y - v_y t / R)^2}{4 \alpha_y v_y t / R} - \frac{(z - v_z t / R)^2}{4 \alpha_z v_z t / R} \right] \exp(-\lambda t) \quad (4.16)$$

Where

- M_0 = the mass of contaminant introduced at the point source
- α_x = dispersivity in the X direction
- α_y = dispersivity in the Y direction
- α_z = dispersivity in the Z direction
- x = distance in X direction from the center of the contaminant mass
- y = distance in Y direction from the center of the contaminant mass
- z = distance in Z direction from the center of the contaminant mass

- V = volume of the contaminant mass
- n_e = the effective porosity
- λ = first order degradation
- t = time

5 Flow in the Unsaturated Zone

5.1 Water content in soil

The unsaturated zone occurs between the water table and the ground surface. With the exception of parts of the capillary fringe, the pores contain both water and soil gases. The quantity of water in a partially saturated medium can be represented in terms of the volumetric water content (θ), which is defined as

$$\theta = \frac{V_w}{V_T} \quad (5.1)$$

Where V_T is some unit volume of soil or rock, and V_w is the volume of water. If the pore is completely saturated, the volumetric water content is equal to the porosity (n). Therefore, in the unsaturated zone, water contents vary over the range, $0 \leq \theta \leq n$. Furthermore, the degree of saturation can fluctuate depending upon variables such as weather, vegetation, and management.

5.2 Retention of water in soil

Water is retained in unsaturated soil by the forces of capillarity (generated by cohesive forces between water molecules) and adsorption (generated by adhesive forces between water molecules and soil particles). These forces act in the opposite direction to the gravitational force, which tends to drain water from the soil. In a soil containing both water and air, water will generally adsorb more strongly to the soil particles and essentially surround them, while air tends to stay in the middle of the pore spaces. The two phases are separated by interfaces across which discontinuities in pressure exist. The existence of interfaces is a characteristic phenomenon occurring when two or more immiscible fluids or phases exist in the pore spaces.

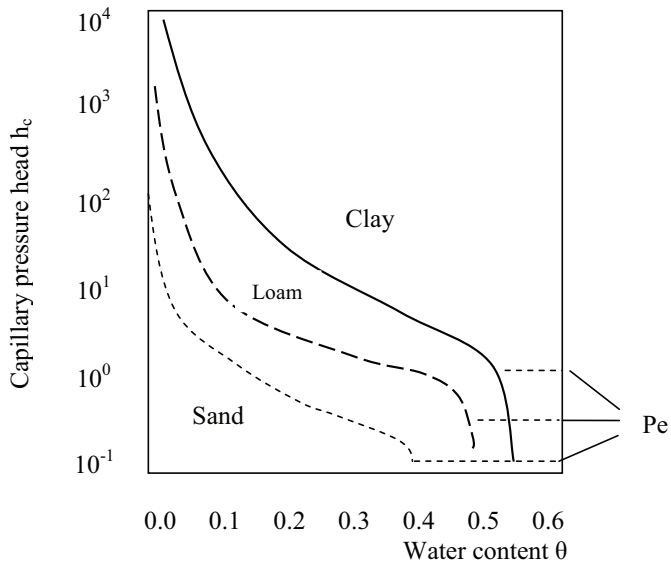


Fig. 5-1. Water- retention curves (Capillary pressure as a function of water content (retention curve)) (Jensen 2001).

Higher capillary pressures or smaller radii of curvature are accompanied by a change in water distribution. Corresponding values of water content θ or saturation and capillary pressure h_c are shown in figure 5-1.

A characteristic property of this relationship is the air- entry pressure, p_e , which is the suction that must be exceeded before air can enter the soil and initiate the de-saturation process. From the curves shown in the figure 5-1, it can also be seen that sandy soils release more water at low suctions than more clay-based soils. Furthermore, a soil of uniform particle size distribution releases most of the water at a small range of suction.

The retention curve can be obtained in two ways, either by (1) drainage: where an initially saturated sample is allowed to de-saturate while the suction is increased; or (2) by wetting: where an initially dry soil sample allows adsorbing water while the suction is reduced. Each

of these two procedures results in curves of different shape, known as the drying and wetting curves, respectively (Fig. 5-2).

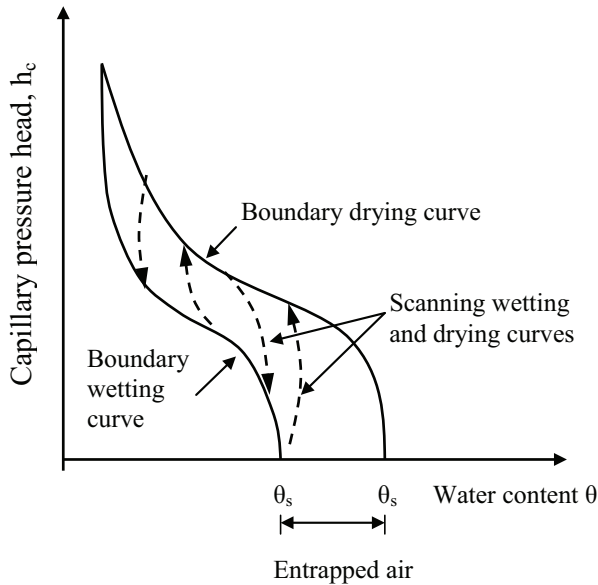


Fig. 5-2. Qualitative illustration of the wetting and drying curves (Jensen 2001).

5.3 Unsaturated hydraulic conductivity

A fundamental relationship in unsaturated water flow is the hydraulic conductivity function between hydraulic conductivity k and water content θ . The conductivity function possesses the characteristic feature of decreasing strongly as θ decreases from its saturated value. An example of the $k(\theta)$ function for different soil types which all display the rapid decrease in hydraulic conductivity with decreasing water content is shown in figure 5-3 (Alfnes *et al.* 2004).

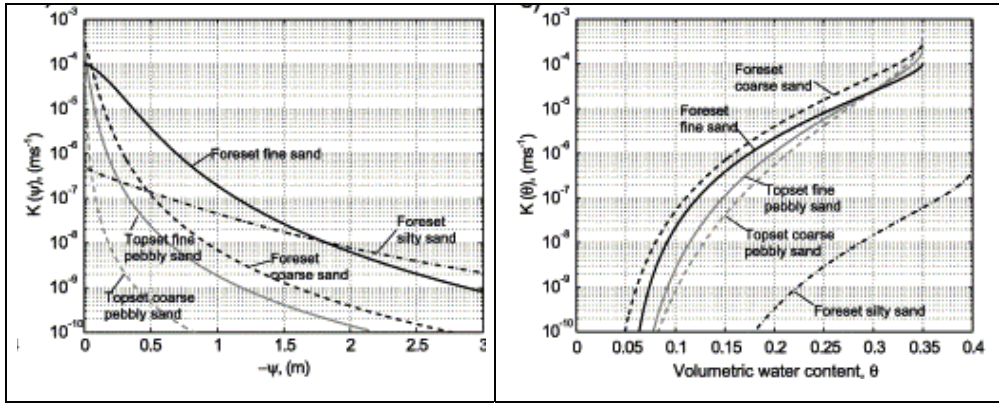


Fig. 5-3. Hydraulic conductivity k , as a function of pressure potential ψ , and volumetric water content θ (Alfnes *et al.* 2004).

5.4 Soil water potential

Soil water potential is a measure of the energy status of the soil water. It reflects how hard plants must work to extract water. Soil water potential is negative pressure (tension or suction). Water flows from a high (less negative) potential to a lower (more negative) potential.

Using the unit of length for the potential functions the total potential is called “hydraulic head”, and is defined as:

$$h(\theta) = z + \psi(\theta) \tag{5.2}$$

Where z is the elevation head and ψ is the pressure head ($P/\rho_w g$). However, the pressure heads in the unsaturated zone are less than atmospheric pressure.

The driving force for water flow in the soil water zone is given by:

$$\Delta h(\theta) = \Delta z + \Delta \psi(\theta) \tag{5.3}$$

Where Δ is the symbol for the gradient operator.

The driving forces for the movement of soil water are described by the gradient of the hydraulic head function. The resulting volumetric flux q related to the driving forces producing the motion is known as Buckingham-Darcy's law, and is written as

$$v_D = q = -k(\theta) \frac{\Delta h(\theta)}{\Delta z} \quad (5.4)$$

Alfnes *et al.* (2004) presented the relationship between pressure potential ψ and volumetric water content θ in the Gardermoen ice-contact delta in Norway (**Fig. 5-4**).

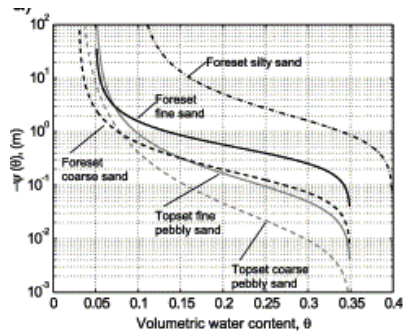


Fig. 5-4. Pressure potential ψ as a function of volumetric water content θ . (Alfnes *et al.* 2004)

5.5 Contaminant transport in unsaturated zone

The transport equation to solve for contaminant transport in the unsaturated zone has the same form as Eq. 4.16, but now both the hydraulic conductivity as well as the hydraulic head are functions of water saturation.

6 Contaminants in Soil

6.1 Soil and contaminants

A large quantity of different chemicals is used at the surface of the earth in our daily life. The chemicals can infiltrate the unsaturated zone by precipitation and gravity. Soil is both a porous material through which solutions and suspensions can move, and a high absorbent material that preferentially adsorbs molecules and particles from solution or suspension. Soil acts as a filter and a buffer, and has a large degradation potential with respect to storage of pollutant with the help of soil organic carbon (Buraue and Bassmann 2005). On the other hand, soil is also a potential pathway of chemical transport to water, plants, and the human

food chain. When contaminants exceed the retention capacity in the unsaturated zone, they can reach the groundwater and spread further into the aquifer.

The main driving forces in contaminant transport in soils are advective and diffusive in nature. Advective flow can be described by groundwater flow models, and dispersion of molecules during advective flow will depend on several constraints dictated by the pore geometry and the continuity of the porous media (soil), as well as the hydrogeological setting. The characteristics of soils in the landscape will determine the flow of water (Yong *et al.* 1992).

Water solubility and adsorption to soil are important in determining the contaminants tendency to move through the soil profile with infiltrating water, and over the soil with runoff. The remainder is retained in the soil and continues to be available for plant uptake, degradation, or leaching. How much of the contaminants that meet each of these fates depends on many factors, including (Trautmann *et al.* 2007):

- The properties of the contaminant
 - ✓ Solubility
 - ✓ Volatilization
 - ✓ Adsorption (K_d , K_{oc})
 - ✓ Degradation
- The properties of the soil
 - ✓ Soil texture
 - ✓ Soil permeability
 - ✓ Soil organic matter content
 - ✓ Soil structure, including macropores
- The site conditions, including:
 - ✓ Depth to groundwater
 - ✓ Geologic conditions
 - ✓ Topography
 - ✓ Climate and irrigation practices
- Management practices

6.2 Oil leakage and migration

In industrialized countries hundreds of thousands gasoline storage tanks are buried at filling stations, and many thousands of kilometres of underground pipelines carry petroleum products across continents. It is not surprising, therefore, that leakage and spills from these sources are an increasing threat to groundwater quality.

Contamination of groundwater by petroleum products from leaky tanks or from oil piles has its own characteristics. A non-aqueous liquid phase with lesser or greater density than water is called Light Non-Aqueous Phase Liquids (LNAPL), or Dense Non-Aqueous Phase Liquids (DNAPL). The oil or the gasoline normally is less dense than water and immiscible in water, so they are called LNAPLs. Figure 6-1 illustrates the main subsurface migration stages that occur when oil seeps into the ground.

In the first migration stage, the oil movement is primarily downward under the influence of gravitational forces. During this seepage stage, capillary forces produce some lateral migration. This causes a zone, referred to as the *oil-wetting zone*, around the core of the infiltrating body. It is comparable in origin to the natural capillary fringe on the water table. In the *oil-wetting zone*, the degree of oil saturation decreases outwardly and capillary forces (surface tension) are dominant. In the main seepage zone, only gravitational forces exist (Freeze and Cherry 1979).

The second stage is when the seepage front reaches the water table, where the downward seepage of oil ceases. Experimental and field evidence indicates that considerable migration occurs within the capillary fringe at or very near the water table. Since oil is immiscible and is less dense than water, it will float on the groundwater and may slightly depress the water table.

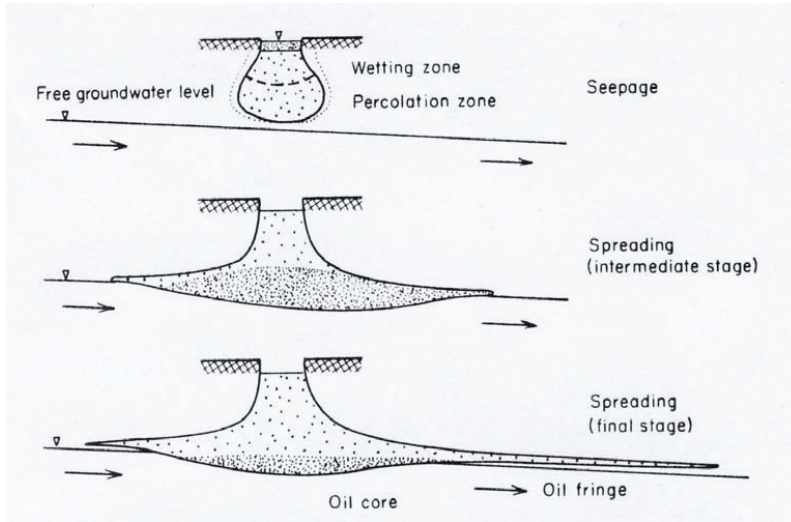


Fig. 6-1. Stages of migration of oil seeping from a surface (Schwille 1967).

However, contemporary mass with separate phase migration, vaporization and dissolution of some of the oil compounds will occur, transferring part of the oil to gaseous and aqueous phases. The dissolved aqueous portion is fed into the groundwater and further transported with the groundwater flow (third stage).

6.3 Contaminant transport in porous medium:

In porous medium, advection, dispersion / diffusion, and reaction are the governing processes for contaminant transport (Appelo 2005). A general 1-Dimensional expression for the reactive advection-dispersion equation is given by:

$$\frac{\partial C}{\partial t} = \frac{D_L}{R} \frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R} \frac{\partial C}{\partial x} - \lambda C \quad (6.1)$$

Where

- C = the solute concentration of the contaminant (mg/l);
- D_L = the hydrodynamic dispersion coefficient in the longitudinal direction (m²/year)
- v_x = the pore water velocity (m/year)
- R = the retardation factor

λ = the first-order decay constant

While most of water movement in soils occurs when both water and air are present in the voids, the value of hydraulic conductivity k is no longer constant but decreases as the water content decreases, or as the soil-water potential ψ decreases. Two parameters, k and D (diffusivity) are used to describe the velocity in the unsaturated zone for one-dimensional flow (Eq. 6.2 and 6.3) (Yong *et al.* 1992).

$$v_D = -k(\theta) \frac{\partial \psi}{\partial z} \quad (6.2)$$

$$v_D = -D(\theta) \frac{\partial \theta}{\partial z} \quad (6.3)$$

6.4 Contaminants under study

Three main categories of contaminants have been applied to probability methods in this thesis. One category is pesticides, many of which are persistent in nature. The other two categories are glycols and jet-fuel, which are used in large quantities at airports in colder climates. Glycols and jet-fuel have different water solubility, but they are both biodegradable. Glycols have almost no retardation, while the water soluble compounds in jet-fuel (such as toluene) are retarded.

Pesticide

Pesticides are any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating a pest. Pesticides also include herbicides, fungicides, and various other substances used to control pests. In 2005, an investigation concerning the use of pesticides in agriculture was carried out by the Norwegian Statistical Bureau (Statistics Norway). The results indicated that the use of pesticides increased by 12 % from 2001 to 2003, and decreased slightly by 1 % to 2005. The total use of pesticides in agriculture is approximately 350 tonnes, with minor changes from 2003 to 2005. Figure 6-2 shows the results of the investigation of the amounts of pesticides used in Norway in 2001, 2003 and 2005, and table 6-1 indicates three pesticides' distributions in areas growing different crops (SSB 2006).

Pesticides are useful to society; they can kill potential disease-causing organisms and control insects, weeds, and other pests. On the other hand, pesticides can cause harm to humans, animals, or the environment because they are designed to kill or otherwise adversely affect living organisms.

Some pesticides are very persistent in soil, break down slowly and are a source of contamination for a long time (Matthews 2006). They can adversely affect the local groundwater (EPA 1996; Goncalves *et al.* 2007; Martins *et al.* 2007; Scorza *et al.* 2007; Tariq *et al.* 2007; USGS 1998). Pesticides, such as DDT, 2,6-dichlorobenzamide, bentazon and dichlorprop have also been reported in groundwater in Norway (Haarstad and Ludvigsen 2007). Clean-up of soils and groundwater contaminated by pesticides is often very difficult, and the contamination may last for many years.

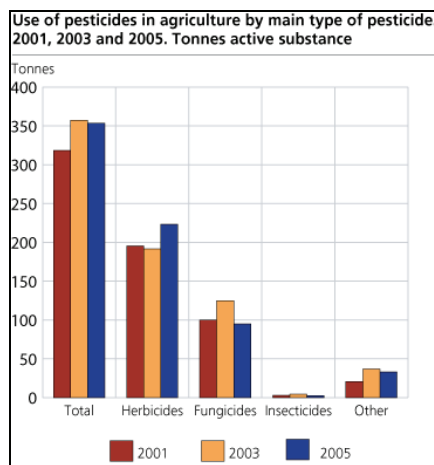


Fig. 6-2. In Norway, the use of pesticides increased by 12 % from 2001 to 2003, and decreased slightly by 1 % to 2005. Of the total use of pesticides, herbicides accounted for 63 % and fungicides 27 %. Figure 6-2 shows the main types of pesticides used in agriculture in Norway in 2001, 2003 and 2005. Investigation was carried by Norwegian Statistical Bureau, 2006.

Table 6-1. Results of investigation of type of pesticides usage distribution on area of different crop in Norway, 2005.

	Area sprayed. Decares	Percent of area sprayed with:				
		Herbicides	Fungicides	Insecticides	Growth regulators	Defoliant
Potato	132 540	91	93	35	-	59
Onion	6 602	98	85	26	-	-
Cabbage	4 790	75	4	89	-	-
Carrot	12 181	97	59	72	-	-
Strawberry	16 022	80	91	85	-	-
Apple	12 556	41	84	11	-	-
Meadows for mowing and pastures	368 221	5	-	-	-	-
Barley	1 516 555	92	52	9	22	-
Oats	655 312	89	:	3	8	-
Spring wheat	517 079	97	76	27	26	-
Winter wheat	265 687	96	88	18	57	-
Oil-seeds	53 909	51	7	65	-	5

Toluene

Toluene, also known as methylbenzene or phenylmethane, is a clear liquid, with low water solubility, and having a typical smell like that of paint thinners. It is an aromatic hydrocarbon that is widely used as an industrial feedstock and as a solvent. Toluene is also one of the main components of many petroleum products.

The United States Environmental Protection Agency (EPA) found that when people are exposed to toluene at levels above the Maximum Contaminant Level (MCL) for relatively short periods of time, it will cause minor nervous system disorders such as fatigue, nausea, weakness, and confusion. If exposure levels exceed the MCL, toluene has the potential to cause more pronounced nervous disorders such as spasms, tremors, impairment of speech, hearing, vision, memory, coordination, and liver and kidney damage.

Toluene is released into the atmosphere principally from the volatilization of petroleum fuels, toluene-based solvents and thinners, and from motor vehicle exhaust. It is also released in waste water or by spills on land during the storage, transport and disposal of fuels and oils.

From 1987 to 1993, according to EPA's Toxic Chemical Release Inventory, releases of toluene to land and water totaled over 4 million pounds, primarily from petroleum refining industries (EPA 2006).

Toluene released to soil will be lost by evaporation from near-surface soil and by leaching down to the groundwater. Its breakdown by soil microbes is rather slow. Toluene evaporates within a few hours when released to water, and it has little tendency to accumulate in aquatic life (Iannuzzi *et al.* 2004).

Propylene glycol (PG)

Propylene glycol (PG), known also as propane-1, 2-diol, is an organic compound (a diol alcohol), usually a faintly sweet, colourless clear viscous liquid that is hygroscopic and miscible with water, acetone, and chloroform. Contact with PG may cause irritation, erythema, vomiting, respiratory tract irritation, and central nervous system depression, while the oral toxicity of propylene glycol is very low. Serious toxicity will occur only at extremely high levels of intake over a relatively short period of time that results in plasma concentrations of over 4 g/L. The Material Safety Data Sheet warns users to avoid skin contact with propylene glycol as this strong skin irritant can cause liver abnormalities and kidney damage.

In airfields, propylene glycol is used as airplane de-icer. A typical de-icer contains 80-90% glycols by weight (Cancilla *et al.* 1997). In Oslo Gardermoen airport, Norway, the total consumption of propylene glycol was 2850, 1000 and 1093 tonnes in the winters of 1998/1999, 1999/2000, and 2000/2001, respectively. The de-icing chemicals can degrade under unsaturated conditions. Degradation rates and travel times through the unsaturated zone determine whether the de-icing chemicals reach the groundwater or not (French *et al.* 1999).

7 Results

Based on understanding of FORM/SORM methodology and contaminants transport in pore medium, we studied the contamination risk of five pesticides in groundwater, and the contamination risk to both saturated and saturated zones if jet- fuel lines / tanks are accidentally broken. Following are the brief results of these studies.

Paper 1

In this study, we considered five pesticides: DDT, bentazon, mecoprop, metribuzin and propiconazole, covering a range in water solubility and octanol-water partition coefficient (K_{ow}). Starting with the contaminants' concentration in soil, we predicted the probabilities of pesticides exceeding critical levels in groundwater, by combining the first order reliability method (FORM) with analytical solutions to a dilution/transport model (SFT 1999) of contaminant migration through the unsaturated zone and further in groundwater.

Contaminant transport in an aquifer is an integrated process which depends on chemical and physical characteristics and aquifer conditions. The soil concentration C_s , organic carbon-water partition coefficient K_{oc} and Henry's constant H are the most important parameters contributing to failure probability of the groundwater when the aquifer conditions are uniform.

The risk of contaminating groundwater is highly dependent upon which executive standard of critical concentration level is applied. One feature evident in figure 7-1 is that, for a certain critical level, the failure probability increases very fast in a certain range of pesticide concentrations in soil, and the failure probability changes slowly beyond these ranges. Therefore, it is necessary to construct a reference diagram to show these differences, especially for policy makers when considering local water usage or evaluating environmental risk.

Our results also indicate that the importance factors' distributions are similar in the failure probability range of approximately 5% to 99.9%, dependent on the critical level applied for the same pesticide. If the failure probability is very small (i.e. < 5%) or very large (i.e. >99.9%), the importance factors will ultimately be controlled by one or several parameters. Importance factors' distribution in groundwater for the five pesticides, with failure probabilities approximated to be 50% and critical levels assigned according to the 98/83/EC water quality standard, was indicated in the paper (Fig. 7-2). The authors also showed the importance factors' distribution for DDT under four critical levels, and a case study with propiconazole as an example.

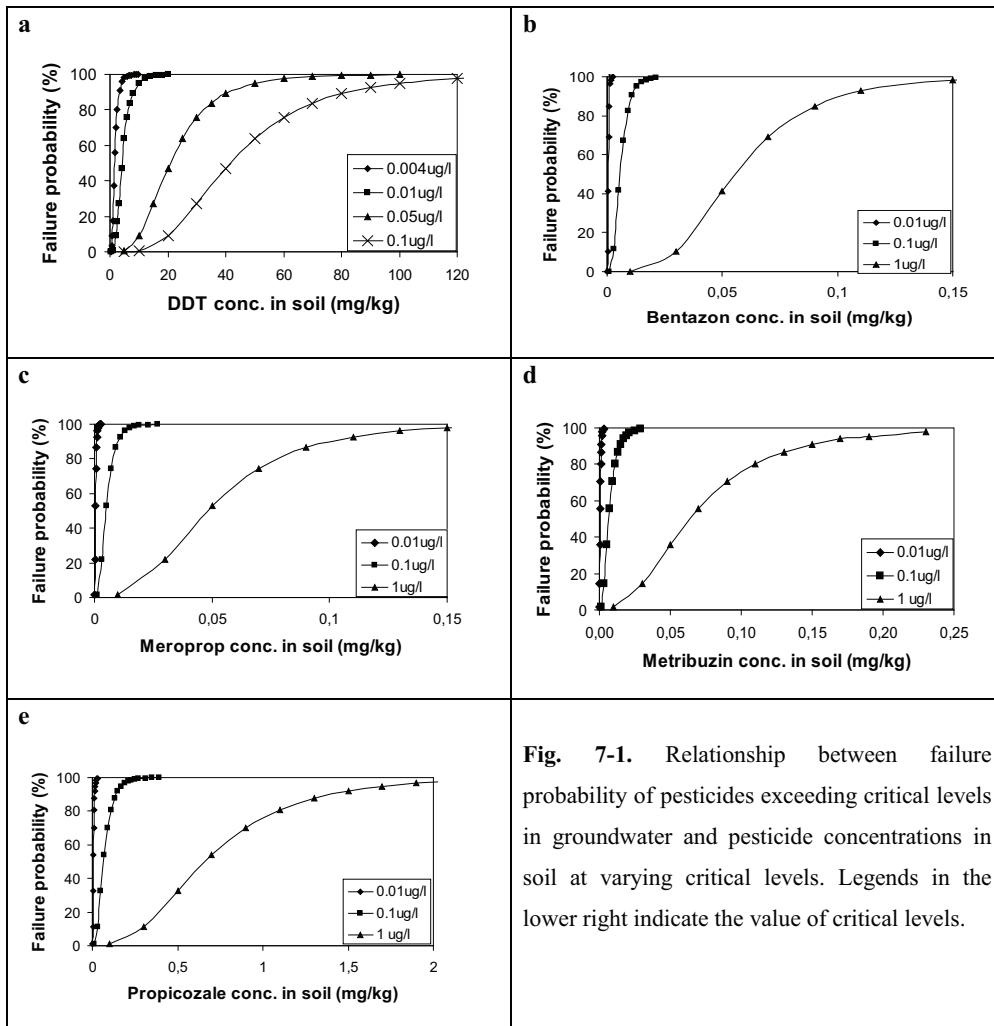


Fig. 7-1. Relationship between failure probability of pesticides exceeding critical levels in groundwater and pesticide concentrations in soil at varying critical levels. Legends in the lower right indicate the value of critical levels.

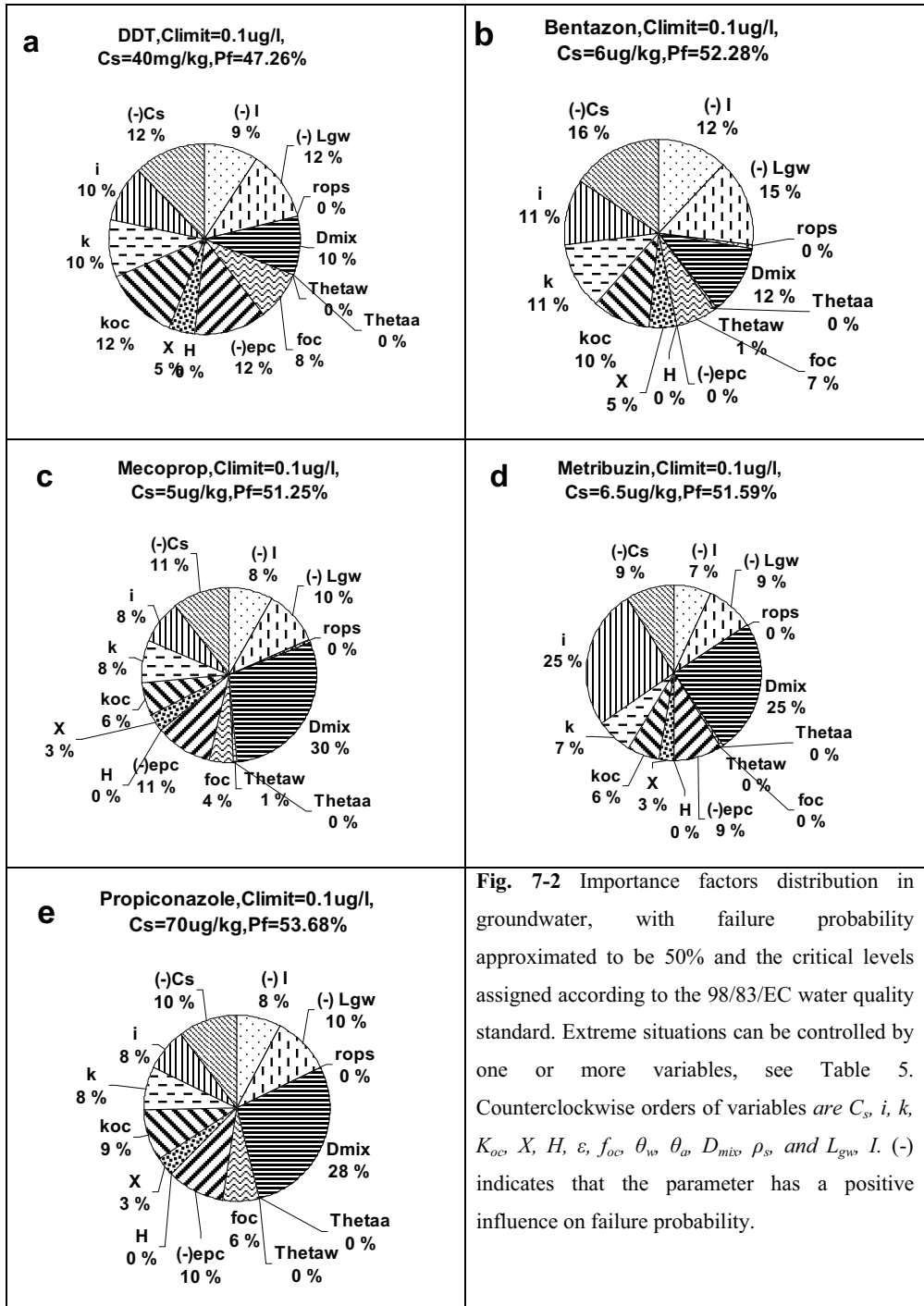


Fig. 7-2 Importance factors distribution in groundwater, with failure probability approximated to be 50% and the critical levels assigned according to the 98/83/EC water quality standard. Extreme situations can be controlled by one or more variables, see Table 5. Counterclockwise orders of variables are C_s , i , k , K_{oc} , X , H , ε , f_{oc} , θ_w , θ_a , D_{mix} , ρ_s , and L_{gw} . I . (-) indicates that the parameter has a positive influence on failure probability.

Paper 2

Jet-fuel leakage and the use of de-icing chemicals in cold weather are two main potential sources of contamination that threaten the groundwater around airports. Combining the First Order Reliability Method (FORM) and the contaminant transport equation, the probability of contaminant concentration in groundwater exceeding critical levels was obtained in time and space for two accident scenarios, continuous release and instantaneous injection. In the scenarios considered, the retention capacity in the unsaturated zone was exceeded, so that the contaminants reached the groundwater and spread further down - gradient into the aquifer. Biodegradation and time were considered in the paper, which made this research extend further than the first paper. The importance factors were identified by sensitivity analysis.

There are many uncertainties when contaminants enter the subsurface as a result of accidental spread or leakage from containers and pipes. Generally, we have no prior knowledge of where an accident may take place, and therefore site specific hydrogeologic model parameters are not available. But, on the other hand, we know what accidents might occur. According to experience and existing knowledge and data, we can have some knowledge of potential accidents. Considering this, we defined “no-information” and “part-information” scenarios according to the information we were able to obtain. For instance, we cannot know exactly how much jet fuel will enter the subsurface when an accident happens. But on the other hand, we can predict or calculate this value before or after the accident happens, based on experience and scientific data. To deal with these parameters, we designed two scenarios that could occur. One is that the leakage, whether continuous or instantaneous, occurs completely unknown. This is referred to as a “no-information” scenario. However, sometimes one has some information about the accident. We can then partly determine the value of these parameters, at least to some extent. After measurement or evaluation, for example, the leaked jet fuel is estimated to be around one ton; we define it as a normal distribution and give it a standard deviation as 20% of the mean value, so the amount of jet-fuel is from 0.8 to 1.2 tonnes. This is referred to as a “part-information” scenario.

Two key compounds in jet fuel and de-icing chemicals, toluene and propylene glycol (PG), have been used to assess the pollution risk to local groundwater. In this paper, failure probabilities of exceeding a critical level of toluene and propylene glycol were predicted.

The probabilistic sensitivity of the probability with respect to various uncertainty parameters was also evaluated and expressed in the form of importance factors.

In the first case, continuous release of contaminants, with both “no-information” and “part-information” of the leakage were studied. Results show (**Fig. 7-3**) that in the “no-information” leakage scenario, failure probabilities of both toluene and propylene glycol decrease gently and contaminate larger areas than in the “part-information” leakage scenario. Failure probability in the “no-information” leakage scenario was shown to be smaller than that in the “part-information” leakage scenario when close to the contaminated sites. After a certain distance, the failure probability will show the opposite results.

Sensitivity analysis is quantified through various parameters’ importance factors. One phenomenon is similar to the scenarios described in the first paper (Zhang *et al.* 2009b): when failure probabilities are either very small or very large, the importance factors are normally controlled by one or a few variables. Sensitivity analysis of the “part-information” of leakage scenario shows a different trend than for the “no-information” scenario.

Deterministic results are also calculated by the contaminant transport equation, in order to compare these with the results from the probabilistic prediction. Results indicated that the concentration of toluene is about 0.01 mg/L (critical level concentration) at 3.6 m, when $C_0 = 22$ mg/L, and the concentration of PG is 0.1 g/L (critical level concentration) at 42 m, when $C_0 = 20$ g/L. The failure probabilities of toluene that are predicted by FORM are 80% and 46% at 3.6 m for the “no-information” and “part-information” of leakage scenarios, respectively. The failure probabilities of propylene glycol are 82% and 57% at 42 m for the “no-information” and “part-information” of leakage scenarios, respectively. Deterministic methods which need point estimates to represent input parameters often use average values of parameters. This may either lead to the exposure concentration being over-estimated or under-estimated. Probabilistic methods, which use uncertainties’ distribution of parameters, can more truly reflect a real situation.

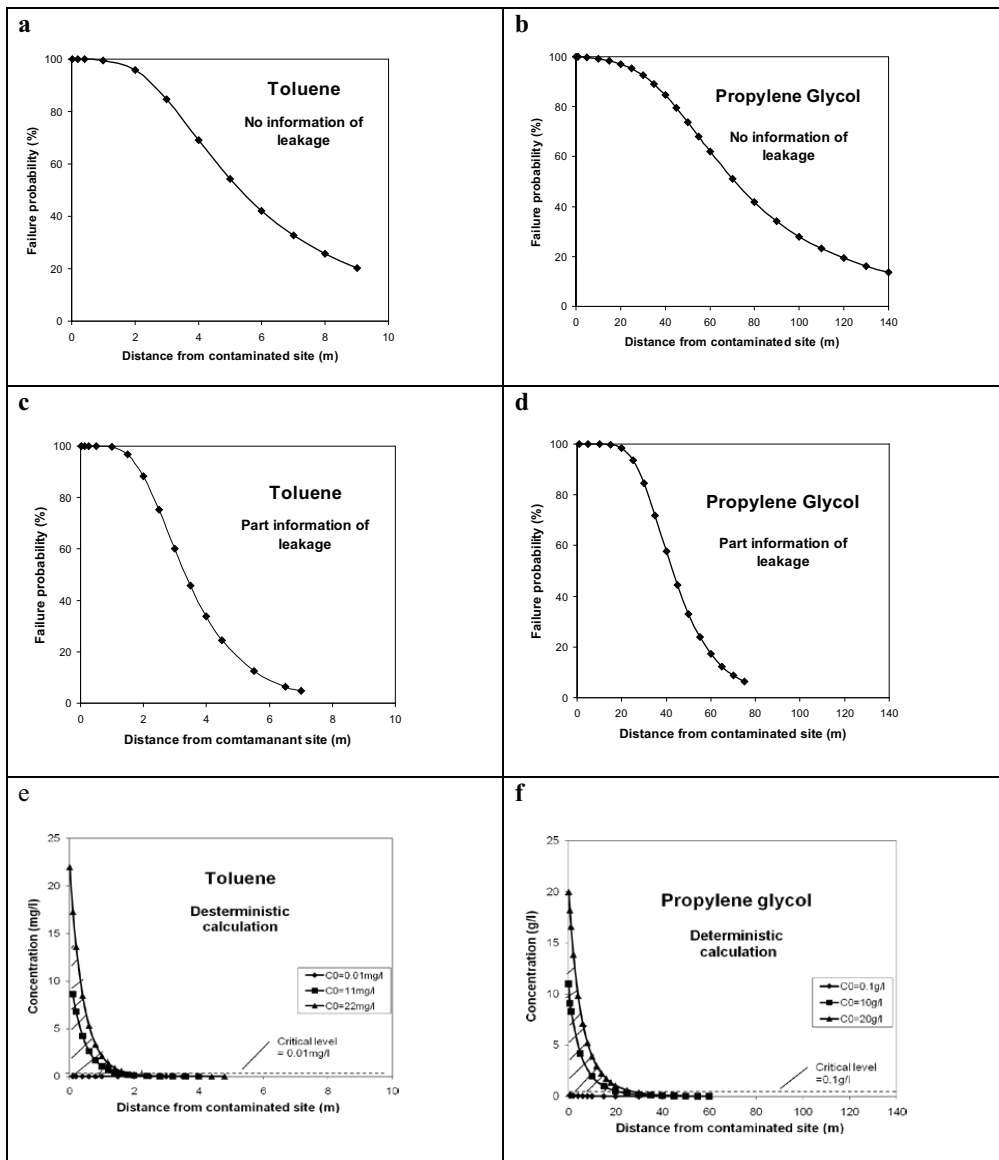


Fig. 7-3. Failure probabilities of toluene and PG predicted by the FORM method in continuous release for the “no-information” and “part-information” of leakage scenarios. Deterministic calculation indicates the concentration in groundwater with C_0 from low boundary to high boundary in probabilistic prediction. The values of the distances in the figure indicate high boundary in the “no-information” of leakage scenario, and mean value in the “part-information” of leakage scenario.

In the second case study, that of instantaneous injection, we hypothesized a scenario where a tank of jet fuel above the groundwater table spills due to an accident, causing leakage of up to but less than one tonne of jet fuel. Results indicate that, in general, the FORM method predicted that the maximum failure probabilities will move further away from the source of contamination with time, and the peaks become lower and lower. This phenomenon corresponds to the results calculated by the deterministic method (**Fig. 7-4**).

Failure probabilities predicted by the FORM method can be compared with results from deterministic calculation. For instance, deterministic calculations show that after 3 months, the toluene plume travelled 6.5 m down flow, and the concentration reduced to 0.01mg/L (the critical level used in the FORM). Corresponding failure probabilities predicted by FORM in both the “no-information” and “part-information” leakage scenarios are 73% and 75%, respectively, for the same time (3 months) and distance (6.5m). In figure 7-3, we can see a large peak in the deterministic calculation for three months before 5.5m, corresponding to the failure probabilities predicted by the FORM method, 75% for the “no-information” and 90% for the “part-information” leakage scenarios, respectively.

Sensitivity analysis was evaluated by using toluene at three months for both the “no-information” and “part-information” leakage scenarios. In “no-information” situations, the influence of time T increases at the beginning but then decreases rapidly as the distance increases. The influence of distance from the contaminated site x , on the contrary, decreases at first, then increases rapidly as distance increases, while other parameters’ importance factors remain stable and insignificant. After 12 m, the importance factors of T and x are similar, and become the dominant importance factors. For “part-information” leakage situations, sensitivity analysis indicated that the influence of x increases rapidly as distance increases, but the importance factors of other parameters, λ , v , K_d , α , T , ρ and θ , decrease. And finally, x becomes the dominant importance factor.

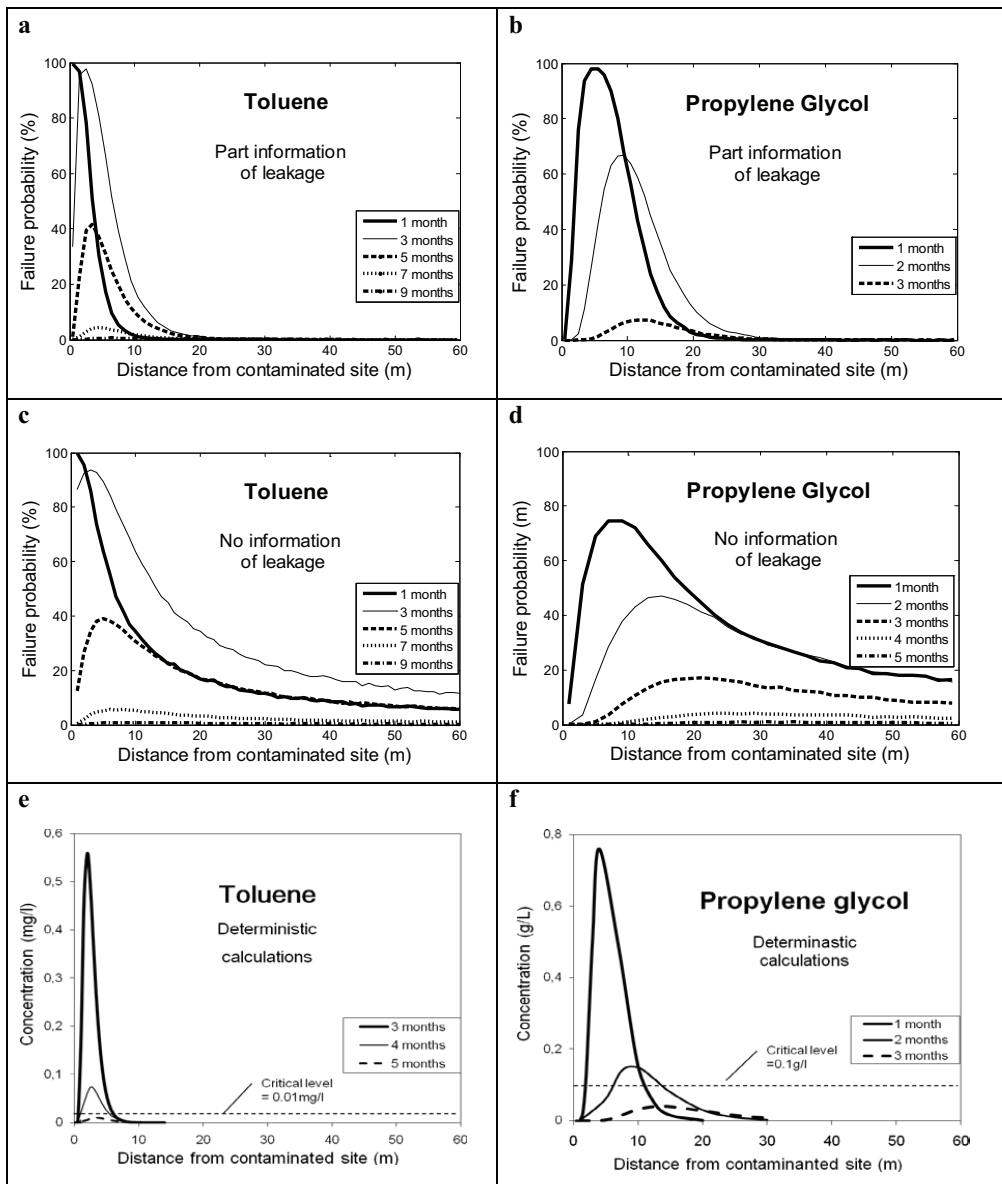


Fig. 7-4. Failure probabilities of toluene and propylene glycol under “no-information” and “part-information” scenarios of instantaneous injection. Results of deterministic calculations are also indicated.

Paper 3

In this study, we combined the transport equation with a probabilistic method, First Order Reliability Method (FORM), to predict the probabilities of toluene exceeding critical levels in the unsaturated zone, if a railway carriage of jet fuel suddenly spilled into the earth. Compared to the saturated zone (Zhang *et al.* 2009a), the biggest challenge in the unsaturated zone is that the water flow velocities vary with water saturation. Numerical solution to the Richards' Equation is then needed.

Following an oil leakage on the ground or within the upper subsoil (buried pipe leakage, etc.), the oil contaminants will spread further in the unsaturated zone by advection, dispersion, adsorption, volatilization (neglected this process in this study) and biodegradation. Large amounts of released oil may cause separate non-aqueous phase flow, while smaller amounts may be residually trapped in the unsaturated zone and not reach down to the groundwater level. We consider the last scenario, where a sudden spill of jet-fuel takes place on the ground. The areal extent of the contaminated area is simulated by the sharp-interface model. The jet-fuel is trapped within the upper part of the unsaturated zone, but the water soluble components will move downward in the water phase. The water velocity in the unsaturated zone is calculated using the Richards' equation and different scenarios of precipitation/infiltration. Combining the mass transport equation with the FORM method, the probabilities of toluene exceeding a critical level in unsaturated zone were predicted as a function of time and space.

According to meteorological records, we considered three different scenarios in the study: the precipitation (P) within 24hours is 25mm, 50mm or 100mm, respectively. On the basis of Richards' Equation, and by applying the MultiPhysics programme, corresponding infiltration velocities were obtained.

Results showed that when 150kg of toluene was spilled at the surface, the probability of toluene concentration exceeding 0.01mg/l was zero for the groundwater level of 10 m if P = 25 mm/24hours; and less than 60% for the groundwater level of 5 m. Corresponding simulations of failure probability are depicted in figure 7-5 for when P = 50 mm and 100 mm/24h.

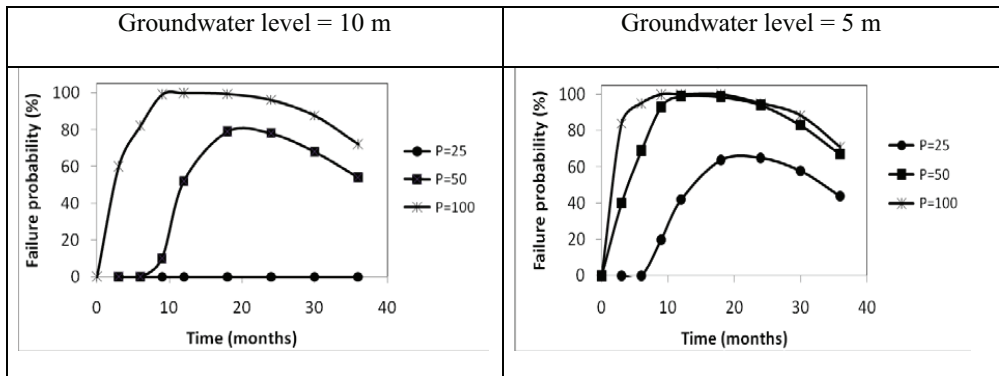


Fig. 7-5. Failure probabilities & time when groundwater levels are 10m and 5m. P represents precipitation (mm) in past 24 hours.

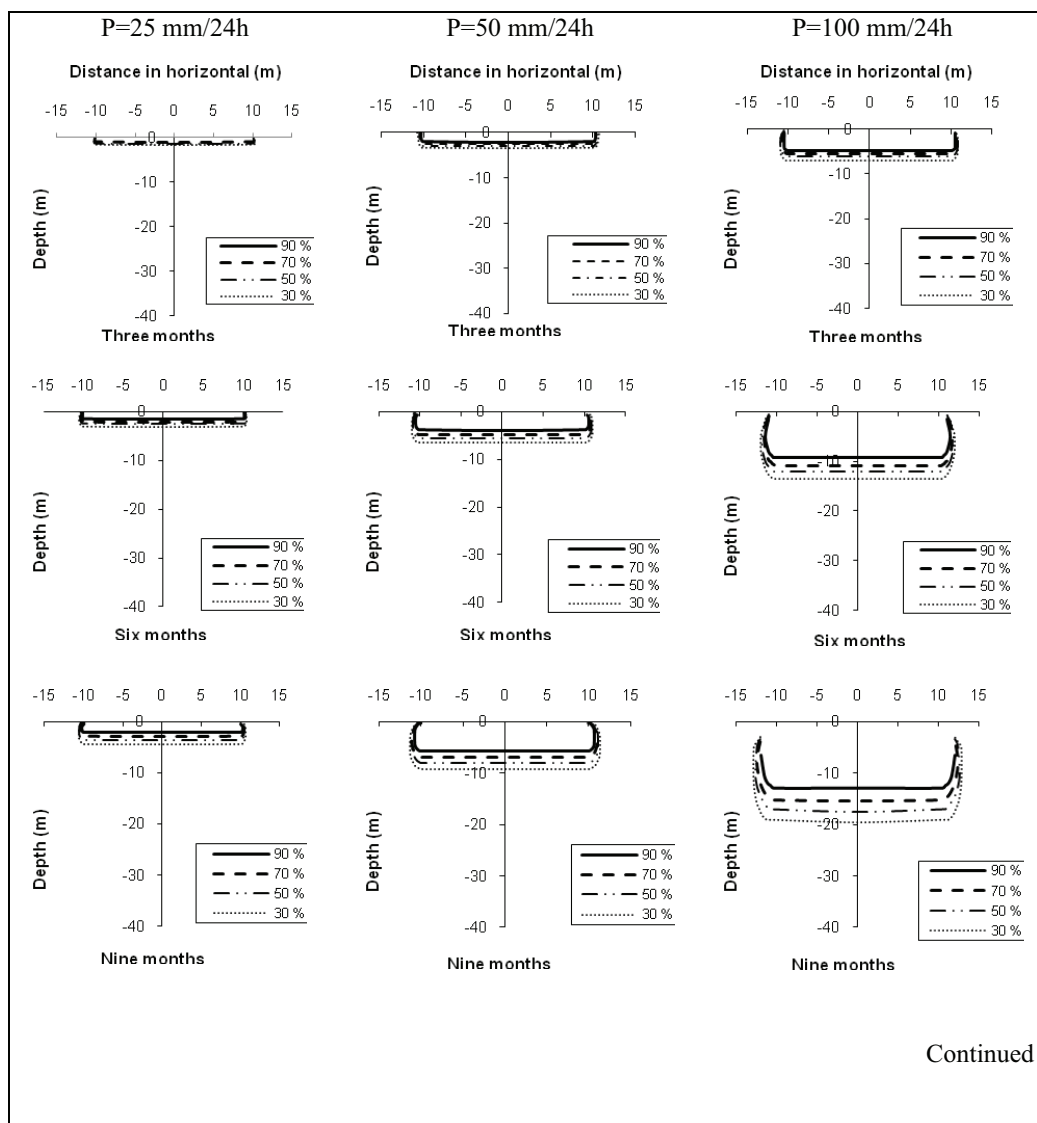
When 150kg of toluene is released and spread within two minutes, the initial horizontal extent of the contaminant plume was calculated by the sharp interface model. Compared to the size of the contaminated area, the initial spreading in the vertical direction was limited, so this was omitted from the figure 7-6. This figure also shows the front plume of the contaminant spreading in the unsaturated zone. Failure probability contours of 30%, 50%, 70% and 90% were predicted for various times and amounts of precipitation.

During the first three months of leakage, the contaminants are concentrated/ convergent in the contaminated site. After three months, the failure probability contour will gradually expand with depth and horizontal distance with time, and the contaminated areas will increase. After one year, the 90% contour line ceased to grow larger and the furthest distances were 2.8 m, 7 m and 16 m for precipitation amounts of 25 mm, 50 mm and 100 mm/24hour, respectively. The 30%, 50% and 70% lines continue to grow larger in both the vertical and horizontal directions, and with higher precipitation, the contaminated area becomes larger. The function of biodegradation starts to appear at this time. These phenomena can also be shown in the sensitivity analysis later. After three years, the risk of contamination decreases. The 90% and 70% lines disappear and the 50% and 30% areas also decrease. There is minimal risk that the contamination will move further into the groundwater.

Sensitivity analysis indicated that the most influential importance parameters are pore water velocity v_z , retardation R , and biodegradation λ . The influence of v_z and R will decrease with time. Velocity has more influence in cases of lower precipitation than in higher precipitation,

while sorption has more influence in higher precipitation. The influence of biodegradation increases with time. After one year, the importance factor of λ increased sharply (Fig. 7-7).

The comparison between deterministic calculation and probabilistic prediction proves further that the deterministic method can only give a YES/NO answer. Probabilistic methods, to the contrary, because they consider the uncertainties, can give more comprehensive and objective conclusions. This can be more practical in environmental risk assessment.



Continued

Continue

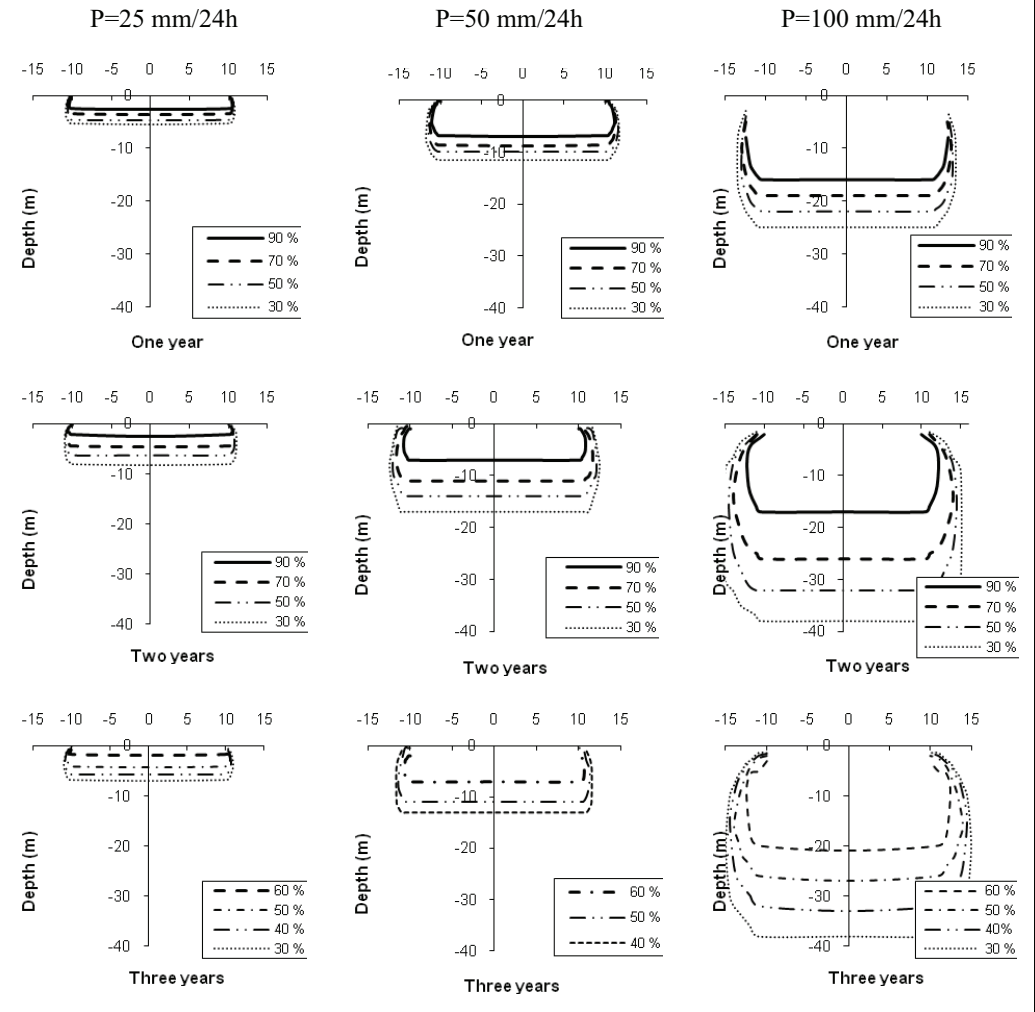


Fig. 7-6. Failure probability changes with time and distance in the unsaturated zone. P represents precipitation (mm) during the past 24 hours. The legend represents the failure probability.

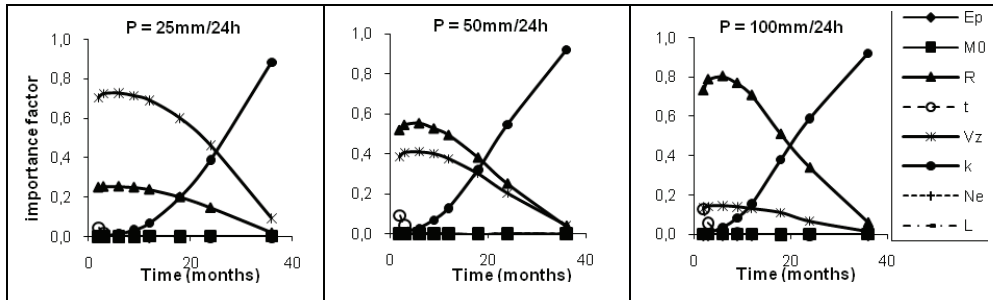


Fig. 7-7. Distribution of importance factors for various precipitations (P). E_p represents modeling uncertainty; M_0 represents amount of contaminant; R represents retardation, t represents time; v_z represents velocity in the vertical direction; λ represents first-order biodegradation constant; N_e represents effective porosity, and L represents the diameter of the contaminated area.

8 Conclusions and future perspectives

Groundwater plays, and will continue to play a critical role in the water cycle globally and in satisfying water requirements locally. Thus, sustainable groundwater development and protection of groundwater quality should receive more attention. Risk assessment can effectively predict contamination risk and further propose suggestions to the authorities in order to avoid or reduce pollution. Large uncertainties are an inherent part of the risk assessment process that have to be dealt with. Probabilistic risk assessment methods can be applied to characterizing variability and uncertainty in certain exposure scenarios, and to indicating how large an influence the input variables have on the risk being assessed. One thereby can improve the risk management and decision-making process. This study has applied a probabilistic approach to the environmental impact assessment of groundwater (and the unsaturated zone). The important advantage of using a probabilistic approach is that it accounts for uncertainties more explicitly and transparent for decision makers.

The First Order Reliability Method (FORM), in combination with analytical solutions to a transport model of contaminant migration in groundwater, easily and effectively predicted the probability of a contaminant exceeding a critical level. Scenarios considering both with and without degradation, continuous and instantaneous injection of contaminants, “no-information” and “part-information” of leakage, were studied for groundwater contaminant risk. For the complicated unsaturated zone conditions, the unstable parameters, such as water velocity, were resolved by integrating the use of a variety of models, to further predict the contaminant risk to the groundwater. In this study, we also calculated the contaminants’

concentration by using a deterministic method. Compared to the probabilistic method, the deterministic calculation may give false assurance, because it sometimes underestimates the hidden contaminants' risk.

Contaminants released at the surface must pass through the unsaturated zone before being spread into the groundwater. There is no theoretical analytical approach for connecting unsaturated zone and saturated zone transport. To calculate the combined failure probability, one needs to apply the series system probabilistic method. This approach has been promoted in this study.

In this thesis, failure probability as function of time and distance and importance factors distribution are expressed by simple figures, which clearly indicate the contaminants' risks distribution and the variables' contribution to the failure probability. This provides a clear and simple summary of the main risks and can provide transparency and directly offer suggestions for decision-makers. Hence, the authorities can easily find how dangerous the situation is and which factors are most important so that they may take action and reduce the risk of groundwater contamination. Despite these important advantages in risk assessment, there is still need for improvement. Further work is necessary in the following areas:

- Basically, we considered the contaminant source as a point, to predict its contaminant probability. However, for long distance transport of oil, several points of leakage may occur at the same time. In this situation, the plumes of pollution and the failure probability (contaminant concentration exceeding a critical level) may or may not overlap. Whether the approach can be further extended and applied to such cases needs to be further studied.
- We selected some typical chemicals, which are common in agriculture and industry, for study in this thesis. This can reflect some problems but is limited. Hundreds and thousands chemicals are being used in our daily lives. It is a great challenge to find a simple method for considering all of the chemicals in order to provide more convenient tools for predicting environmental risk.

- We used standard deviations of 20% of the mean value for most of the parameters in this study. This is a simple and convenient way to cope with parameters when there is a lack of information about them, yet it also brings imprecise prediction. For instance, as mentioned in paper II, the distribution of importance factors depends on the position of the parameters in the transport equation and also the parameter uncertainty. Different standard deviations will change the importance factors' distribution to some extent. Therefore, more work is needed to further constrain the parameter uncertainty.
- In the unsaturated zone study, we introduced numerical models to successfully cope with two main key parameters: the pore water flow velocity and the radial extent of contaminant spreading. We realized that more work is needed in order to deal with more complex scenarios when combining numerical simulations with analytical models.

9 References

- (2004). "Implementation of SEA Directive (2001/42/EC): Assessment of the Effects of Certain Plans and Programmes on the Environment, Guidelines for Regional Authorities and Planning Authorities." <http://www.environ.ie/en/Publications/DevelopmentandHousing/Planning/FileDownload,1616,en.pdf>, last accessed date: 12-08-2009.
- ADB. (1997). *Environmental Impact assessment for Developing Countries in Asia*, Asia Development Bank (ADB).
- Alfnes, E., Kinzelbach, W., and Aagaard, P. (2004). "Investigation of hydrogeologic processes in a dipping layer structure: 1. The flow barrier effect." *Journal of Contaminant Hydrology*, 69(3-4), 157-172.
- Alshuwaikhat, H. M. (2005). "Strategic environmental assessment can help solve environmental impact assessment failures in developing countries." *Environmental Impact Assessment Review*, 25(4), 307-317.
- Appelo, C. C. A. J. (2005). *Geochemistry, groundwater and pollution / C.A.J. Appelo, D. Postma*.
- Apul, D., Gardner, K., Eighmy, T., Linder, E., Frizzell, T., and Roberson, R. (2005). "Probabilistic modeling of one-dimensional water movement and leaching from highway embankments containing secondary materials." *Environmental Engineering Science*, 22(2), 156-169.
- Bekesi, G., and McConchie, J. (1999). "Groundwater recharge modelling using the Monte Carlo technique, Manawatu region, New Zealand." *Journal of Hydrology*, 224(3-4), 137-148.
- Bindu N.Lohani, J. W. E., Robert R. Everitt, Harvey Ludwig, Richard A. Carpenter, Shih-Liang Tu. (1997). *Environmental Impact Assessment for Developing Countries in Asia*, Asian Development Bank.

- Binkowitz, B. S., and Wartenberg, D. (2001). "Disparity in quantitative risk assessment: A review of input distributions." *Risk Analysis*, 21(1), 75-90.
- Biswas, A. K. (1992). "**Environmental impact assessment for groundwater management** " *International Journal of Water Resources Development* <<http://www.informaworld.com/smpp/1141940655-750067/title~db=all~content=t713426247>>, 8(2), 113-117.
- Blanset, D. L., Zhang, J. F., and Robson, M. G. (2007). "Probabilistic estimates of lifetime daily doses from consumption of drinking water containing trace levels of N,N-diethyl-meta-toluamide (DEET), triclosan, or acetaminophen and the associated risk to human health." *Human and Ecological Risk Assessment*, 13(3), 615-631.
- Boateng, S., and Cawfield, J. D. (1999). "Two-dimensional sensitivity analysis of contaminant transport in the unsaturated zone." *Ground Water*, 37(2), 185-193.
- Bogardi, I., and Ducksteinz, L. "The fuzzy logic paradigm of risk analysis." *10th United-Engineering-Foundation Conference on Risk-Based Decisionmaking in Water Resources*, Santa Barbara, CA, 12-22.
- Cancilla, D. A., Holtkamp, A., Matassa, L., and Fang, X. C. (1997). "Isolation and characterization of microtox(R)-active components from aircraft de-icing/anti-icing fluids." *Environmental Toxicology and Chemistry*, 16(3), 430-434.
- Cawfield, J. D., and Wu, M. C. (1993). "Probabilistic Sensitivity Analysis for One-Dimensional Reactive Transport in Porous-Media." *Water Resources Research*, 29(3), 661-672.
- Chen, G. Z., Hsu, K. C., and Lee, C. H. (2003). "Probabilistic assessment of contamination using the two-phase flow model." *Waste Management & Research*, 21(4), 367-376.
- Cizelj, L., Mavko, B., and Rieschoppermann, H. (1994). "Application of 1st and 2nd- Order Reliability Methods in the Safety Assessment of Cracked Steam-Generator Tubing " *Nuclear Engineering and Design*, 147(3), 359-368.
- Dimakis, P. (1997). "Reliability Analyses of Groundwater Pollutant Transport [Ph.D thesis]," University of Oslo, Oslo.
- EPA. (1996). "Pesticides and Ground Water State management Plan Regulation, June 26, 1996 (Volume 61, Number 124)."
- EPA. (1999). "Supplemental Guidance to RAGS (RAGS III Part A): The use of probabilistic Analysis in Risk Assessment, working draft. Office of Emergency and Remedial Response, Washington, DC 20460. April 1999."
- EPA. (2000). "Superfund Probabilistic Risk Assessment to Characterize Uncertainty and Variability." U.S. Environmental Protection Agency, U.S.A.
- EPA. (2006). "Consumer Factsheet on: TOLUENE,." http://epa.gov/OGWDW/contaminants/dw_contamfs/toluene.html, last date access: 04-09-2009.
- EPA. (2009). "Risk Assessment Portal - Glossary." U.S. Environmental Protection Agency, U.S.A.
- ESPO. (2003). "European Spatial Planning Observation Network (ESPO): Glossary of Terms." <http://www.gsf.fi/projects/espon/glossary.htm>, last accessed 14-06-2009
- EUROPA. (2009). "Groundwater." http://ec.europa.eu/environment/water/water-framework/groundwater/deterioration/index_en.htm, laste access date: 15-09-2009.
- Fairman, R., D.Mead, C., and Williams, W. P. (1998). *Environmental Risk Assessment: Approaches, Experiences and Information Sources*, EEA (European Environment Agency) London.
- FAO. (2002). "Food and Agricultural Organization (FAO), FAO/WHO global forum of food safety regulators, Country report proposed by Iran, Marrakech, Morocco, 28-30

- January (2002) " [ftp://ftp.fao.org/docrep/fao/meeting/004/ab428e.pdf](http://ftp.fao.org/docrep/fao/meeting/004/ab428e.pdf), last accessed 23-05-2007.
- Fetter, C. W. (1988). *Applied hydrogeology*, Merrill Publ. Co., Columbus, Ohio.
- Freeze, R. A., and Cherry, J. A. (1979). *Groundwater*, Prentice-Hall, Englewood Cliffs, N.J.
- French, H. K., van der Zee, S., and Leijnse, A. (1999). "Differences in gravity-dominated unsaturated flow during autumn rains and snowmelt." *Hydrological Processes*, 13(17), 2783-2800.
- Gaganis, P., and Smith, L. (2008). "Accounting for model error in risk assessments: Alternatives to adopting a bias towards conservative risk estimates in decision models." *Advances in Water Resources*, 31(8), 1074-1086.
- Garrick, B. J. (2002). "The use of risk assessment to evaluate waste disposal facilities in the United States of America." *Safety Science*, 40(1-4), 135-151.
- Gilpin, A. (1995). *Environmental impact assessment (EIA): cutting edge for the twenty-first century*, Cambridge University Press, Cambridge.
- Goncalves, C. M., Esteves da Silva, J. C. G., and Alpendurada, M. F. (2007). "Evaluation of the pesticide contamination of groundwater sampled over two years from a vulnerable zone in Portugal." *Journal of Agricultural and Food Chemistry*, 55(15), 6227-6235.
- Grenney, W. J., Caupp, C. L., Sims, R. C., and Short, T. E. (1987). "A Mathematical-Model for the Fate of Hazardous Substances in Soil - Model Description and Experimental Results." *Hazardous Waste & Hazardous Materials*, 4(3), 223-239.
- Ham, J. H., Yoon, C. G., Jung, K. W., and Jang, J. H. (2007). "Integrated modelling under uncertainty in watershed-level assessment and management." *Water Science and Technology*, 56(8), 31-39.
- Hamed, M. M. (1997). "First-order reliability analysis of public health risk assessment." *Risk Analysis*, 17(2), 177-185.
- Hamed, M. M., and Bedient, P. B. (1997). "On the performance of computational methods for the assessment of risk from ground-water contamination." *Ground Water*, 35(4), 638-646.
- Hamed, M. M., Conte, J. P., and Bedient, P. B. (1995). "Probabilistic Screening Tool for Groundwater Contamination Assessment." *Journal of Environmental Engineering-Asce*, 121(11), 767-775.
- Hamed, M. M., and El-Beshry, M. Z. (2006). "Application of first-order reliability method to modelling the fate and transport of benzene in groundwater." *International Journal of Environment and Pollution*, 26(4), 327-346.
- Hasofer, A. M., and N.C.Lind. (1974). "Exact and invariant second moment code format." *Journal of the Engineering Mechanics Division, ASCE*, 100, 111-121.
- Huang, H., Hassan, A. E., and Hu, B. X. (2003). "Monte Carlo study of conservative transport in heterogeneous dual-porosity media." *Journal of Hydrology*, 275(3-4), 229-241.
- Haarstad, K., and Ludvigsen, G. H. (2007). *Ten Years of Pesticide Monitoring in Norwegian Ground Water*, Blackwell Publishing.
- Iannuzzi, T. J., Armstrong, T. N., Thelen, J. B., Ludwig, D. F., and Firstenberg, C. E. (2004). "Chemical contamination of aquatic organisms from an urbanized river in the New York/New Jersey Harbor Estuary." *Human and Ecological Risk Assessment*, 10(2), 389-413.
- Isukapalli, S. S. (1999). "Approach for Uncertainty Analysis." <http://www.ccl.rutgers.edu/~ssi/thesis/thesis-node51.html>, last accessed 15-08-2009.
- ITRC. (2005). "Overview of Groundwater Remediation Technologies for MTBE and TBA, prepared by the Interstate Technology & Regulatory Council MTBE and Other Fuel

- Oxygenates Team " www.itrcweb.org/Documents/MTBE-1.pdf
<http://www.itrcweb.org/Documents/MTBE-1.pdf> , last accessed date: 02-07-2009.
- Jang, Y. S., Sitar, N., and Kiureghian, A. D. (1994). "Reliability-Analysis of Contaminant Transport in Saturated Porous-Media." *Water Resources Research*, 30(8), 2435-2448.
- Jensen, K. H. (2001). "Soil Physical Processes." Institute of Hydrodynamics and Hydraulic Engineering (ISVA) Technical University of Denmark.
- Karickhoff, S. W. (1981). *Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils.*, Chemosphere 10, 833-846.
- Kentel, E., and Aral, M. M. (2004). "Probabilistic-fuzzy health risk modeling." *Stochastic Environmental Research and Risk Assessment*, 18(5), 324-338.
- Kinzelbach, W. W. (1986). *Groundwater modelling : an introduction with sample programs in BASIC* Amsterdam : Elsevier.
- Kostecki, P. T., and Calabrese, E. J. (1990). *Petroleum contaminated soils* 3, Lewis Publishers, Chelsea, Mich.
- Kumar, V., and Schuhmacher, M. "Fuzzy uncertainty analysis in system modelling." *15th European Symposium on Computer Aided Process Engineering (ESCAPE-15)*, Barcelona, SPAIN, 391-396.
- Kunstmann, H., Kinzelbach, W., and Siegfried, T. (2002). "Conditional first-order second-moment method and its application to the quantification of uncertainty in groundwater modeling." *Water Resources Research*, 38(4).
- Kvaerner, J., Swensen, G., and Erikstad, L. (2006). "Assessing environmental vulnerability in EIA - The content and context of the vulnerability concept in an alternative approach to standard EIA procedure." *Environmental Impact Assessment Review*, 26(5), 511-527.
- Lahkim, M. B., and Garcia, L. A. (1999). "Stochastic modeling of exposure and risk in a contaminated heterogeneous aquifer. 1. Monte Carlo uncertainty analysis." *Environmental Engineering Science*, 16(5), 315-328.
- Lenntech. (2009). "Sources of groundwater pollution." <http://www.lenntech.com/groundwater>, last accessed date: 02-07-2009.
- Lipton, L. (1996). "Encyclopedia of climate and weather - Schneider,SH." *Library Journal*, 121(10), 94-94.
- Liu, L., Cheng, S. Y., and Guo, H. C. (2004). "A simulation-assessment modeling approach for analyzing environmental risks of groundwater contamination at waste landfill sites." *Human and Ecological Risk Assessment*, 10(2), 373-388.
- Macintosh, D. L., Suter, G. W., and Hoffman, F. O. (1994). "Uses of Probabilistic Exposure Models in Ecological Risk Assessment of Contaminated Sites." *Risk Analysis*, 14(4), 405-419.
- Madsen, H. O., Krenk, S., and Lind, N. (1986). *Method of Structure Safety*, Prentice-Hall.
- Marseguerra, M., and Zio, E. (2001). "Looking at Monte Carlo simulation for describing nonlinear sorption in groundwater contaminant transport." *Mathematics and Computers in Simulation*, 55(1-3), 167-176.
- Martins, E. L., Weber, C. L. S., Dores, F. G. C., and Spadotto, C. A. (2007). "Leaching of seven pesticides currently used in cotton crop in Mato Grosso State - Brazil." *Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes*, 42(8), 877-882.
- Matthes, G. (1989). "Contaminant transport in groundwater: proceedings of the International Symposium on Contaminant Transport in Groundwater." *Stuttgart, 4-6 April 1989*.
- Matthews, G. (2006). *Pesticides: health, safety, and the environment*, Blackwell Publ., Oxford.

- McKone, T. E., and Bogen, K. T. (1991). "Predicting the Uncertainties in Risk Assessment - a California Groundwater Case-Study." *Environmental Science & Technology*, 25(10), 1674-1681.
- McNab, W. W. (2001). "A Monte Carlo simulation method for assessing biotransformation effects on groundwater fuel hydrocarbon plume lengths." *Computers & Geosciences*, 27(1), 31-42.
- Melchers, R. E. (1999). *Structure Reliability Analysis and Prediction*, Ellis Horwood Ltd.
- MERL. (2001). "Manual for Environmental Impact Assessment, Ministry of Environment of the Republic of Lithuania." *Institute of Environment of Finland*.
- Mitchell, T., J., and Cutter, S. L. (1997). "Global Change and Environmental Hazards: Is the World Becoming More Disastrous? ." *Association of American Geographers*. <<<http://www.aag.org/hdgc/www/hazards/units/unit1/html/unit1frame.html>>>, last accessed date 04-07-2009.
- MMC. (2002). "Parameters for an Independent Study To Assess the Future Benefits of Hazard Mitigation Activities. Multihazard Mitigation Council (MMC): Washington, DC: ." *National Institute of Building Sciences (July)*. <<<http://www.nibs.org/MMC/images/July%202002%20Phase%201%20Final%20Report.pdf>>>, last accessed date 24-06-2009.
- OECD. (2006). "Applying Strategic Environmental Assessment, Good Practice guidance for Development Co-operation." <http://www.oecd.org/dataoecd/4/21/37353858.pdf>, last accessed date: 15-08-2008.
- Perneczky, L. (2008). "Good Examples of EIA and SEA Regulation and Practice in Five European Union Countries - Justice & Environmenta (2008), The report was funded by the European Commission - LIFE+ programme." Brno, Czech Republic.
- Pimentel, D. (1995). "Amounts of Pesticides Reaching Target Pests - Environmental Impacts and Ethics." *Journal of Agricultural & Environmental Ethics*, 8(1), 17-29.
- Plimmer, B. R. (1998). "The use of a top down probabilistic modelling approach to contaminant transport." *Geoenvironmental Engineering*, 248-253.
- Risse, N., Crowley, M., Vincke, P., and Waaub, J.-P. (2003). "Implementing the European SEA Directive: the Member States' margin of discretion " *Environmental Impact Assessment Review*.
- Rong, Y., Wang, R. F., and Chou, R. (1998). "Monte Carlo simulation for a groundwater mixing model in soil remediation of tetrachloroethylene." *Journal of Soil Contamination*, 7(1), 87-102.
- Ryall, Á. (2005). "EIA Law - the State of the Art." <http://www.ucc.ie/law/events/environ05papers/>, last accessed date, 15-09-2009.
- Sarang, A., Vahedi, A., and Shamsai, A. (2008). "How to quantify sustainable development: A Risk-based approach to water quality management." *Environmental Management*, 41(2), 200-220.
- Schneiderbauer, S., and Ehrlich, D. (2004). "Risk, hazard and people's vulnerability to natural hazards." *A review of definitions, concepts and data. European Commission Joint Research Centre. EUR 21410 EN. 40 pp.*
- Schwarzenbach, R. P., and Westall, J. C. (1985). "Sorption of hydrophobic trace organic compounds in groundwater systems." *Water Science and Technology*, 17, 39-55.
- Schwille, F. (1967). *Petroleum contamination of the subsoil - a hydrological problem*.
- Scorza, R. P., Jarvis, N. J., Boesten, J., Van der Zee, S. E., and Roulier, S. (2007). "Testing MACRO (version 5.1) for pesticide leaching in a Dutch clay soil." *Pest Management Science*, 63(10), 1011-1025.
- Selvadurai, A. P. S. (2002). "The advective transport of a chemical from a cavity in a porous medium." *Computers and Geotechnics*, 29(7), 525-546.

- Senecal, P., Sadler, B., Goldsmith, B., Brown, K., and Conover, S. (1999). "Principles of Environmental Impact Assessment Best Practice, International Association for Impact Assessment." *the leading global network on impact assessment*, http://www.iaia.org/modx/assets/files/Principles%20of%20IA_web.pdf, last accessed date: 15-08-2009.
- SFT. (1999). "Guidelines for the Risk Assessment of Contaminated Sites." 99:06, Norwegian Pollution Control Authority, Oslo.
- Skaggs, T. H., and Barry, D. A. (1997). "The first-order reliability method of predicting cumulative mass flux in heterogeneous porous formations." *Water Resources Research*, 33(6), 1485-1494.
- Smith, R. L. (1994). "Use of a Monte-Carlo Simulation for Human Exposure Assessment at the Superfund Site." *Risk Analysis*, 14(4), 433-439.
- SSB. (2006). "Increased use of herbicides, Statistisk Sentralbyrå Bureau (Norwegian statistics bureau)." <http://www.ssb.no/english/>, last accessed date, 05-06-2009.
- Tariq, M. I., Afzal, S., Hussain, I., and Sultana, N. (2007). "Pesticides exposure in Pakistan: A review." *Environment International*, 33(8), 1107-1122.
- Thwih, M., and Mar, T. T. (2002). "Current status of pesticides residue analysis of food in relation with food safety
- FAO/WHO Global Forum of Food Safety Regulators - GF CRD Myanmar-1
<ftp://ftp.fao.org/docrep/fao/meeting/004/ab429e.pdf>.
- Trautmann, N. M., S. Porter, K., and J. Wagenet, r. (2007). "Natural Resources Cornell Cooperative Extension, Pesticides and groundwater: A Guide for the Pesticide User." <http://pmep.cce.cornell.edu/facts-slides-self/facts/pest-gr-gud-grw89.html>, last accessed date: 18-09-2008
- USGS. (1998). "Pesticides in Surface and Ground Water of the United States: Summary of Results of the National Water Quality Assessment Program (NAWQA), Pesticides National Synthesis Project, National Water-Quality Assessment." *U.S. Geological Survey, July 22, 1998*. <http://ca.water.usgs.gov/pnsp/allsum/>, last accessed date: 18-09-2008
- Vinten, A. J. A., Potts, J., Avery, L., and Strachan, N. J. C. (2009). "Microbial pollution of water by livestock: approaches to risk assessment and mitigation." *Animal*, 3(5), 744-752.
- Wittwer, J. W. (2004). "Monte Carlo Simulation Basics." <http://www.vertex42.com/ExcelArticles/mc/MonteCarloSimulation.html>, last accessed date: 19-05-2009.
- Wong, W. K. (2003). "Contaminant migration and its risk mapping in the subsurface - the case of Gardermoen, Norway.," Doctor Scientiarum, University of Oslo, Oslo.
- Wood, C., and Therivel, R. (2006). "Need for SEA: limitation of EIA." Strategic Environmental Assessment, Open Educational Resource, http://sea.unu.edu/course/?page_id=30, last accessed date: 06-02-2009.
- Yong, R. N., Mohamed, A. M. O., and Warkentin, B. P. (1992). *Principles of contaminant transport in soils*, Elsevier, Amsterdam.
- Zhang, P., Aagaard, P., and Gottschalk, L. (2009a). "Probability method used in predicting contaminant risk in airport groundwater." *submitted*
- Zhang, P., Aagaard, P., Nadim, F., Gottschalk, L., and Haarstad, K. (2009b). "Sensitivity Analysis of Pesticides Contaminating Groundwater by Applying Probability and Transport Methods " *Integrated Environmental Assessment and Management*, 5(3), 414-425.
- Öberg, T., and Bergback, B. (2005). "A Review of Probabilistic Risk Assessment of Contaminated Land (12 pp)." *Journal of Soils and Sediments*, 5(4), 213-224.

Paper 1

**Sensitivity analysis of Pesticides Contaminating Groundwater by
Applying Probability and Transport Methods**

by

Pengxin Zhang[†], Per Aagaard[†], Farrokh Nadim^{†‡}, Lars Gottschalk[†], Ketil Haarstad[#]

[†]University of Oslo, NO-0316 Oslo, Norway

[‡]Norwegian Geotechnical Institute, 0806 Oslo, Norway

[#]Bioforsk Soil and Environment, N-1432 Ås, Norway

Published by *Integrated Environmental Assessment and Management*

-----Volume 5, Number 3- pp414-425 ©2009 SETAC

This article is removed.

Paper 2

**Probability method used in predicting contaminant risk
in groundwater adjacent to airport**

by

Pengxin Zhang, Per Aagaard , Lars Gottschalk

(University of Oslo, NO-0316 Oslo, Norway)

Published by *Water, Air and Soil Pollution*

---- DOI 10.1007/s 11270-009-0303-6

This article is removed.

Paper 3

**Application of Probabilistic and Transport Methods to Evaluate
the Contamination Risk in Unsaturated Zone**

by

Pengxin Zhang, Per Aagaard, Lars Gottschalk

(University of Oslo, NO-0316 Oslo, Norway)

Submitted to Environmental Earth Sciences (2009)

This article is removed.

Extension abstract

Risk Assessment of Contaminants in Groundwater

by

Pengxin Zhang, Per Aagaard, Lars Gottschalk

(University of Oslo, NO-0316 Oslo, Norway)

*International Conference on WAter POLLution in nature POrous media at
different scales assessment of fate, impact and indicators. **WAPO²***

BARCELONA (SPAIN) APRIL 11TH-13TH, 2007

RISK ASSESSMENT OF CONTAMINANTS IN GROUNDWATER

PX Zhang¹, P Aagaard¹ and L Gottschalk¹

(1) University of Oslo, P.O. Box 1047, Blindern, NO-316 Oslo, Norway, email: pengxin.zhang@geo.uio.no

ABSTRACT

This paper applies probability methods to study pollution of aquifers. Potential pollution of jet-fuel and de-icing chemicals from air-port activity in cold climate is used as an example of the methodology. The scenario considered, is an exceeding of retention capacity in the unsaturated zone, so the contaminants can reach the groundwater and spread further in the aquifer. The results show that in the first 10 months, the failure probability of toluene (from the jet fuel), i.e. the concentration of the chemicals exceed to a critical level, is more than 90% and can travel 5-13m; after 4 years, this probability is less than 1% and the toluene can reach to 24-60m. The travel distance depends on the properties of contaminants, aquifer materials and velocity of the groundwater. If the groundwater was polluted by propylene glycol (PG), in the first 4 months, the failure probability is more than 90%; after 2years, it will be less than 1%. Having spread with same velocity as the groundwater, since it is not retardation, PG can travel 10- 20m in the first 4months and 80-160 m after 2 years no matter the medium materials.

Key words: contaminant, risk assessment, groundwater

1. INTRODUCTION

Pollution of groundwater by petroleum products and vast number industrial chemicals is recognized as a major threat to the water resources in many areas of the world. Both taste and smell, but not least the toxicity to human beings may destroy groundwater resources (Boyce and Garry, 2003; Nunes-Halldorson et al., 2004; Ritchie et al., 2003). It is thus of outmost importance to have effective methods to predict and reduce the pollution risk. Department of the Environment (1995) represented one of the first attempts to explore some of the underlying principles of assessing environmental risk and contribute to the sustainable development strategy.

Modeling is a key feature of assessing environmental impact. Traditionally, risk assessment on soil and groundwater pollution relies on deterministic analysis (suitable parameters, material properties, geographic conditions etc) and an analysis is then performed to provide a more or less detailed description of the contaminant migration and target exposure. However, when assessing risks, there exist many uncertainties which are not included in a deterministic approach. Probabilistic methods can

provide a powerful method to deal with these problems. The first- and second – order reliability method (FORM and SORM) has been developed in the structural analysis field and has recently been applied to groundwater contaminant transport and the remediation problem (Hamed and Bedient, 1997). With FORM/SORM method, variability and uncertainty in the input parameters (variables and constant) are described by probability distributions, and the output (risk) is likewise presented as a probability of failure in exceeding a critical value.

In this contribution, we have used a potential pollution scenario from running an airport in a cold climate, using the Oslo airport located above the Gardermoen aquifer. Two key compounds, Toluene (from jet-fuel) and Propylene glycol (de-icing chemical), have been used to assess the pollution risk to the local groundwater.

2. METHODOLOGY

Contaminants can migrate through the soil mantle down to the groundwater (Lester and Birkett, 1999) if the retention capacity of the unsaturated zone is exceeded. Several mechanisms control migration of contaminants under both saturated and unsaturated conditions, i.e., advection, dispersion, adsorption/desorption, volatilization, and degradation, including biodegradation (Freeze and Cherry, 1979; Kostecki and Calabrese, 1990).

In this application the focuses is directed toward the transport in groundwater and analytical solution of the transport question is used. The analytical solution is of great service in making first estimates and assessments of a pollutant plum. The required simplifications are homogeneity of the aquifer, parallel flow of constant velocity, constant retardation factors, and dispersivities. Also, the pollutant input must not influence the homogeneous flow field and molecular diffusion is neglected (Kinzelbach, 1986). Consider the one-dimensional case with a first-order degradation term (Freeze and Cherry, 1979; Kinzelbach, 1986).

$$\frac{D_L}{R} \frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R} \frac{\partial C}{\partial x} - kC = \frac{\partial C}{\partial t} \quad (1)$$

For boundary conditions of $C=C_0$ at $x=0$, and $C=0$ as $x \rightarrow \infty$, we can get the solution of Equation 2.

$$\frac{D_L}{R} \frac{\partial^2 C}{\partial x^2} - \frac{v_x}{R} \frac{\partial C}{\partial x} - kC = 0 \quad (2)$$

and
$$R = 1 + \frac{\rho_b K_d}{\theta} \quad (3)$$

where C is the solute concentration of the contaminant (mg/l); D_L is the hydrodynamic dispersion coefficient in the longitudinal direction; v_x is the pore water velocity (m/year); R is the retardation factor; k is the first-order decay constant; θ is the water content of the porous material; K_d is the distribution /partition coefficient (l/kg); ρ_b is the bulk density (1 /m³), equal to 2.65(1- θ); and α_L is the dispersivity (m).

The aqueous concentration of hydrocarbons in equilibrium with an organic phase can be estimated using Raoult's law for ideal solutions (Cline et al., 1991; Lane and Loehr, 1992).

$$C_{i,w} = S_i^0 \cdot X_i \quad (4)$$

where $C_{i,w}$ is the aqueous concentration, X_i is the mole fraction in the organic phase and S_i^0 is the pure component solubility.

First- order biodegradation constant k can be calculated according to equation (5).

$$\frac{dC}{dt} = -kC \quad (5)$$

Distribution/partition coefficient K_d is estimated according to equation 6 and 7 (SFT, 1999).

$$\text{Log } K_{oc} = 1.04 \text{ log } K_{ow} - 0.84 \quad (6)$$

$$K_d = k_{oc} \cdot f_{oc} \quad (7)$$

For the time being less emphasis is put on the uncertainty aspects through unsaturated zone, and for saturated conditions the flow velocity is described by (Equation 8):

$$v = \frac{k}{\theta} \cdot \frac{dh}{dl} \quad (8)$$

where v is the velocity(m/day); θ is porosity; k is hydraulic conductivity(m/day) and dh/dl is hydraulic conductivity(m/day). In Gardermoen area, the gradient varies between 0.01 and 0.007, the effective porosity varies around 0.36. Water moves through the saturated zone with an average velocity of 10-20 cm/day (Jørgensen and Østmo, 1990). This velocity is assumed constant. This assumption will be relaxed in future development.

According to WHO drinking water standard (WHO, 1993) and experts experiences, the maximum contaminant levels are 0.01 mg/l for toluene, and 1g/l for PG, and this level are used to define the probability of failure.

Contrary to the deterministic approach, which uses one single constant value (mean value in general) for each parameter describing soil behaviour, the probabilistic approach considers their variability and defines them using a mean and a standard deviation value. The description of the first- and second-order reliability methods (FORM and SORM methods) can be found in Nadim and Breedveld(2000).

One of the common methods for accounting for uncertainties in physical simulation problems is the Monte Carlo approach. A Monte-Carlo simulation is a procedure, which seeks to simulate stochastic processes by random selection of input values to an analysis model in proportion to their joint probability density function. It is a powerful technique that is applicable to both linear and non-linear problems, but can require a large number of simulations to provide a reliable distribution of the response. This approach becomes computationally intensive when the probability of failure is very small, the number of simulations required to obtain an accurate result directly is so large that, except for very simple (or simplified) problems, it renders the application impractical. In these situations, Monte Carlo simulation can be optimized by stratified sampling and “organized” sampling techniques that considerably reduce the number of simulations required for a reliable distribution of the response. However, the FORM/SORM approach would still be far more efficient when the probabilities of interest are very low because the approximations are focussed on what happens around the most likely failure point, not the complete distribution. Furthermore, obtaining the sensitivity factors from Monte Carlo simulation requires post-processing of the results. For these reasons, the Monte Carlo approach was not used in this study.

The program used for the calculate the failure probability, SYSREL(RCP, 2004), has been designed for the approximate computation of general probability integrals over given domains bounded by unions and/or intersections of individual locally smooth boundaries. It is suited especially for probability integrals occurring in structural reliability but can be used in many other domains. The performance function $g = C_{he} - C_{in situ}$ is used for evaluation of probability of exposure to an

undesirable substance, C_{hc} is the contaminant concentration for receptors and $C_{in\ situ}$ is the actual in situ concentration of the undesirable substance.

3. APPLICATION

Gardermoen airport is located in about 40km north of Oslo. Every day large quantities of jet-fuel are transported to, stored and filled-up into the airplanes in the airport area, and all operations have a certain probability of oil spill into the subsurface. Further more, a number of de-icing chemicals are used on runways and aeroplanes through the winter seasons. Obviously it is a potential source of pollution to the local aquifer. In this study, we use toluene (one compound of jet-fuel) and the de-icing chemical propylene glycol (PG) as examples to assess the risk of groundwater pollution. Initial aqueous concentrations of the two compounds were estimated by: for toluene by Raoult's law and Jet-Fuel compositional data (Smith et al., 1981); for propylene glycol from field experiments (French, 1999; French et al., 2001). Parameters applied in the calculation are shown in table 1.

Table 1 Parameters input

variable	Distribution/value	Data sources
θ	Normal (Variable)	Arbitrary/experience
$C_{0,Toluene}$ (mg/l)	Normal (11, 3.3) ^[1]	(Smith et al., 1981)
$C_{0,PG}$ (mg/l)	Normal (10000, 2000) ^[1]	(French et al., 2001)
$k_{Toluene}$ (year ⁻¹)	Lognormal (20.8, 47.2) ^[1]	(Biggar and Gruber, 2005)
k_{PG} (year ⁻¹)	Normal (11.35, 8.5) ^[1]	(French, 1999)
$Kd_{Toluene}$ (l/kg)	Normal (0.96, 0.24) ^[1]	(Mackay, 2006)
Kd_{PG} (l/kg)	Normal (2.27e-4, 4.45e-5) ^[1]	(Commission, 2000)
ε ^[2]	Normal (1, 0.2) ^[1]	Arbitrary/experience
ε I ^[3]	Normal (1, 0.2) ^[1]	Arbitrary/experience

^[1] (mean value, standard deviation)

^[2] modified parameter for the maximum contaminant levels(RCP, 2004)

^[3] modified parameter for model(RCP, 2004)

4. RESULTS AND DISCUSSION

The failure probability to pollute the groundwater depends to a large extend on the initial concentrations of the contaminant, biodegradation, velocity of the groundwater and K_d .

Failure probability with time From figure 1, we can see in the case of polluting groundwater with jet fuel, the probability of toluene exceeding the critical level in the first 10 months is more than 90%; after 4 years, this probability is less than 1%. If the groundwater was polluted by propylene glycol (PG)(assuming its initial concentration of 10g/l (French, 1999)), the failure probability is more than 90% in the first 4 months, and after 2 years, it will be less than 1% (Fig. 2).

Failure probability with distance The retardation factor of toluene, is 5.5 and 6.61 for values of θ of 0.4 and 0.3, respectively, thus the contaminant will spread accordingly (Fig. 1). For different materials and groundwater velocity, though the failure probability is almost the same at the same time, the travel distance will be quite different (Fig. 1). For toluene in the first 10 months, the probability of exceeding the critical level within a distance of 5-13 m is more than 90%; after 4 years the probability failure is less than 1% past 24–60 m. The travel distance depends on the contaminant properties, aquifer material and groundwater velocity. As PG has no retardation (French, 1999), then θ has no influence on it. The failure probability is more than 90% within 10-20 m for the first 4 months, but this has decreased to less than 1% after 2 years out to 80–160 m (Fig. 2).

5. CONCLUSION

The first- and second order reliability method is, in combination with analytical solutions to the transport equation, a useful method to include uncertainties in input parameters to assess pollution risk of aquifers. We have here applied it for the saturated zone only, neglecting the risk associated with how a surface spill may reach down to the groundwater (Wong, 2003). We will include the unsaturated transport in future developments. The method can also be extended to 2D/3D distributed models, where the spatial heterogeneity will give rise to vulnerability or risk maps.

Failure Probability with Time and Distance(Toluene)

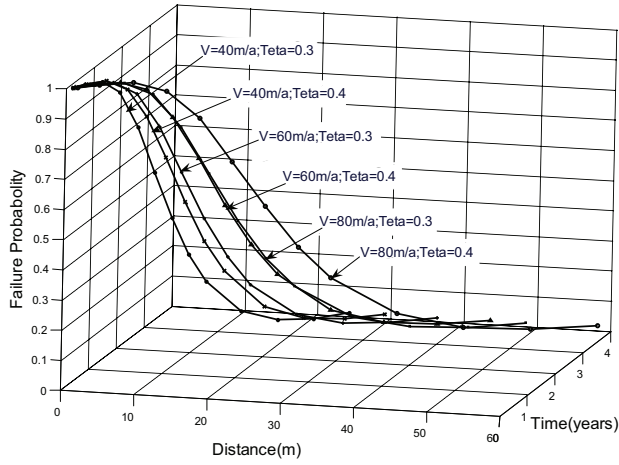


Figure 1 Failure probability of toluene exceeding critical level as a function of time and travel distance

Failure probability with Time and Distance(PG)

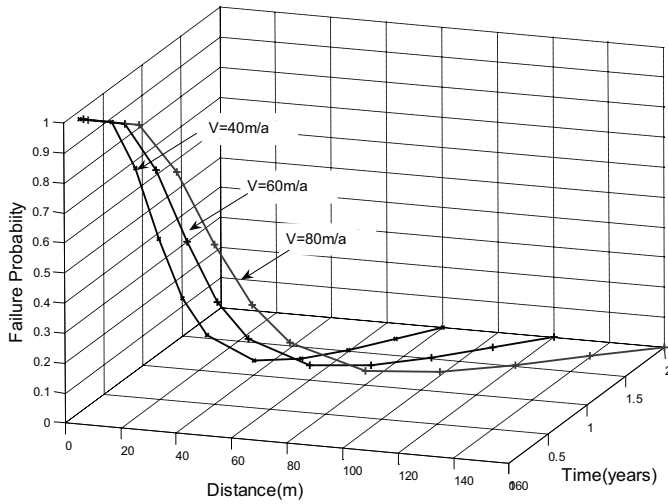


Figure 2 Failure probability of propylene glycol exceeding critical level as a function of time and travel distance

REFERENCE

- Biggar, K. and Gruber, K., 2005. Impact of cold temperatures on biodegradation rates for natural attenuation of petroleum hydrocarbons, University of Alberta Geotechnical Centre, Edmonton.
- Boyce, C.P. and Garry, M.R., 2003. Developing risk-based target concentrations for carcinogenic polycyclic aromatic hydrocarbon compounds assuming human consumption of aquatic biota. *Journal of Toxicology and Environmental Health-Part B-Critical Reviews*, 6(5): 497-520.
- Cline, P.V., Delfino, J.J. and Rao, P.S.C., 1991. Partitioning of Aromatic Constituents into Water from Gasoline and Other Complex Solvent Mixtures. *Environmental Science & Technology*, 25(5): 914-920.
- Commission, E., 2000. IUCLIO Dataset. European Commission European Chemicals Bureau.
- Department of the Environment, 1995. A Guide to Risk Assessment and Risk Management for Environmental Protection London, UK, HMSO.
- Freeze, R.A. and Cherry, J.A., 1979. Groundwater. Prentice-Hall, Englewood Cliffs, N.J., 604 pp.
- French, H.K., 1999. Transport and Degradation of Deicing Chemicals in a Heterogeneous Unsaturated Soil. Agriculture university of Norway, Norway.
- French, H.K., L., B. and Zee, v.e., 2001. Natural attenuation of airport pollutants in the unsaturated zone - studies at Gardermoen, Norway, Current problems of hydro-geology in urban areas, urban agglomerates and industrial centres, Eds: Ken W.F. Howard and Rauf I. Israfilov, Nato Advanced Research Workshop. Kluwer Academic Publishers
- Hamed, M.M. and Bedient, P.B., 1997. On the performance of computational methods for the assessment of risk from ground-water contamination. *Ground Water*, 35(4): 638-646.
- Jørgensen, P. and Østmo, S.R., 1990. Hydrogeology in the Romerike area. *Nor.geol.unders.Bull.*418: 19-26.
- Kinzelbach, W., 1986. Groundwater modelling : an introduction with sample programs in BASIC. *Developments in water science ; 25*. Elsevier, Amsterdam, 333 pp.
- Kostecki, P.T. and Calabrese, E.J., 1990. Petroleum contaminated soils 3. Lewis Publishers, Chelsea, Mich., 423 pp.
- Lane, W.F. and Loehr, R.C., 1992. Estimating the Equilibrium Aqueous Concentrations of Polynuclear Aromatic-Hydrocarbons in Complex-Mixtures. *Environmental Science & Technology*, 26(5): 983-990.
- Lester, J.N. and Birkett, J.W., 1999. Microbiology and chemistry for environmental scientists and engineers. E & FN Spon, London, 386 pp.
- Mackay, D., 2006. Handbook of physical-chemical properties and environmental fate for organic chemicals. Taylor & Francis, Boca Ration.

- Nadim, F. and Breedveld, G.D., 2000. Reliability Analysis of Geoenvironmental Problems. SFT 20001003-1, Oslo, Norway.
- Nunes-Halldorson, V.D., Steiner, R.L. and Smith, G.B., 2004. Residual toxicity after biodegradation: interactions among benzene, toluene, and chloroform. *Ecotoxicology and Environmental Safety*, 57(2): 162-167.
- RCP, 2004. SYSREL:USERS MANUAL. RCP GmbH, Federal Republic of Germany, 60 pp.
- Ritchie, G.D. et al., 2003. Biological and health effects of exposure to kerosene-based jet fuels and performance additives. *Journal of Toxicology and Environmental Health-Part B-Critical Reviews*, 6(4): 357-451.
- SFT, 1999. Guidelines for the Risk Assessment of Contaminated Sites. 99:06, Norwegian Pollution Control Authority, Oslo.
- Smith, J., J.Harper and H.Jaber, 1981. Analysis and Environmental Fate of Air Force Distillate and High Density Fuels, SRI International, Menlo Park, California. October.
- WHO, 1993. WHO's drinking water standards. Lenntech Water treatment & air purification Holding B.V.
- Wong, W.K., 2003. Contaminant migration and its risk mapping in the subsurface - the case of Gardermoen, Norway. Doctor Scientiarum Thesis, University of Oslo, Oslo.

Poster

**The First-order reliability method of predicting Toluene,
Ethylbenzene and Xylene in groundwater**

by

Pengxin Zhang, Per Aagaard

(University of Oslo, NO-0316 Oslo, Norway)

*International Conference on Risk Assessment in European River Basins – State
of the Art and Future Challenges*

KUBUS (UFZ), Leipzig, 12-14 November 2007

The First-order reliability method of predicting BTEX contaminants in groundwater

Pengxin Zhang, Per Aagaard

Contact Person: Pengxin Zhang, email: pengxin.zhang@geo.uio.no,

Tel: 0047-22856688, Fax: 0047-22855269.

Address: P.O.Box1047 Blindern, NO-0316 Oslo, Norway

Abstract

In risk assessment of new and existing hazardous substances, it is current practice to characterize risk using a deterministic quotient of the exposure concentration, or the dose, and a no-effect level. A sense of uncertainty is tackled by introducing worst-case assumptions in the methodology. However, risks often are overestimated in this method and it is difficult to answer “how dangerous”. In addition, when assessing the environmental risks, there are many uncertainties, which the deterministic methods can not deal with. Probability methods can provide a powerful method to deal with these problems. Variability and uncertainty in the input parameters are then described by distributions, and the output is similarly presented as a probability distribution. The first order reliability method (FORM method) has been extensively applied to the probabilistic modelling of engineering structure systems and, also to groundwater transport modelling. By applying the FORM method, the failure probability and sensitivity factors of contaminants reaching the groundwater, can be quantified. In this presentation, we assume a scenario of jet fuel leakage in an airport, percolation to the unsaturated zone, and further spreading in groundwater. By combining groundwater transport model, which includes biodegradation, and the FORM approach, we get the failure probability of BTEX (exceeding the standards of the water quality) in space and time. Sensitivity analysis presents the importance of almost all parameters influence groundwater flowing and identifies the main sources of uncertainty. The application of fuzzy ranking is also included in order to make the uncertainty as explicitly as possible for the decision-makers.



The First-order reliability method of predicting Toluene, Ethylbenzene and Xylene in groundwater

Pengxin Zhang and Per Aagaard

Geoscience department, University of Oslo, P.O.Box 1047, Blindern NO-316 Oslo (Norway) pengxin.zhang@geo.uio.no

Introduction In risk assessment of new and existing hazardous substances, it is current practice to characterize risk using a deterministic quotient of the exposure concentration, or the dose, and a no-effect level. A sense of uncertainty is tackled by introducing worst-case assumptions in the methodology. However, risks often are overestimated in this method and it is difficult to answer "how dangerous". In addition, when assessing the environmental risks, there are many uncertainties, which the deterministic methods can not deal with. Probability methods can provide a powerful method to deal with these problems. Variability and uncertainty in the input parameters are then described by distributions, and the output is similarly presented as a probability distribution. The first order reliability method (FORM method) can be applied to groundwater transport modelling. By applying the FORM method, the failure probability and sensitivity factors of contaminants reaching the groundwater, can be quantified.

Methodology:

I Transportation method

Leakage of oil and other hazardous wastes can migrate through the soil mantle to the groundwater. After reaching the groundwater, the transport equation of one-dimension with first-order degradation is given by:

$$\frac{D_L}{R} \frac{\partial^2 C}{\partial x^2} = \frac{u}{R} \frac{\partial C}{\partial x} - \lambda C = \frac{\partial C}{\partial t}$$

For instantaneous injection of pollutant mass ΔM , the concentration of the contaminant after a certain time is:

$$c_c(x,t) = \frac{\Delta M}{2n_b b m R \sqrt{\pi \alpha u t / R}} \exp\left(-\frac{(x-ut/R)^2}{4\alpha u t / R}\right) \exp(-\lambda t)$$

II First-order reliability method (FORM method)

In the FORM method, a performance function $g(X)$, is defined such that $g(X) \geq 0$ means that the allowable concentration is greater than the exposure concentration (safe state), while $g(X) < 0$ means the opposite (failure state).

The probability of failure Pf is then given as:

$$Pf = P(g(X) < 0) = P(\alpha_i X_i - \beta < 0) = \Phi(-\beta)$$

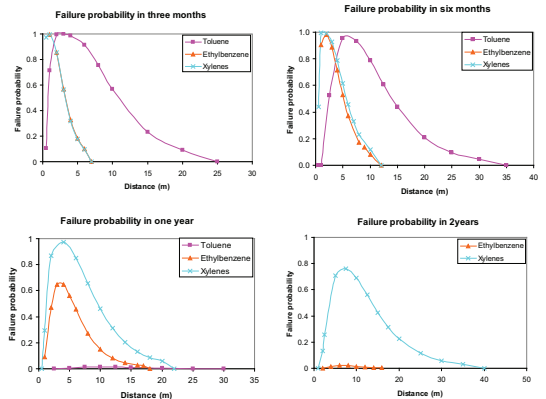
For evaluation of probability of exposure to an undesirable substance,

$$g = C_{\text{limit}} - C_{\text{in situ}}$$

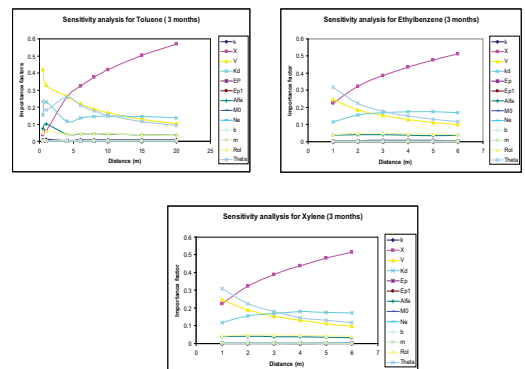
In this presentation, we combine the analytical methods using the transport equation in groundwater with a probability method, the FORM method, in order to estimate the probability of toluene, ethylbenzene and xylenes exceeding standards in space and time.

Results An potential accident of 10 tons jet fuel leakage in an airport was assumed to percolate to the unsaturated zone and further spreading in groundwater. The conditions of this case is simplified as having a homogeneous aquifer, parallel flow of constant velocity, constant retardation factors, reaction rates and dispersivities. Also, the pollutants input does not influence the homogeneous flow field and can be simulated by one-dimensional transport and with first-order degradation. Analysis shows that the failure probability of contaminants, which means the concentration of the toxic chemical exceed the water standards, have the follow characteristics:

I According to the likelihood scales defined by Intergovernmental Panel on Climate Change, $Pf > 66\%$ means likely to happen. In this case, within 2.5m for ethylbenzene and xylenes, and 10m for toluene are likely contaminate the local groundwater within 3months. In 6 months, the same probabilities will travel 5m and 12m respectively. However, with time the failure probability will decrease due to biodegradation. So after one year, toluene very unlikely contaminate the groundwater and the probability of ethylbenzene is less than 66%. After two years, ethylbenzene will very unlikely contaminate the groundwater; while xylenes may still have a probability to contaminate the groundwater between 6-12m.



II Sensitivity analysis shows that after 3 months, the trends of importance factors are similar among toluene, ethylbenzene and xylenes. The importance factor of, distance (X), is more important than other parameters, and it increases with distance. The importance factors of V, θ and Kd are almost in the same importance position, while the important factors of V, θ decrease and Kd increase with the distance.



Input parameters

Variable	Distribution value		
	Toluene	Ethylbenzene	Xylene
Aquifer-related parameters			
θ (m/year)	N (80, 16)	N (80, 16)	N (80, 16)
b (0.35, 0.07)	N (0.35, 0.07)	N (0.35, 0.07)	N (0.35, 0.07)
ρ_s (kg/m ³)	N (1840, 368)	N (1840, 368)	N (1840, 368)
w	N (2, 0.4)	N (2, 0.4)	N (2, 0.4)
m	N (15, 3)	N (15, 3)	N (15, 3)
n_s	N (0.3, 0.06)	N (0.3, 0.06)	N (0.3, 0.06)
Chemical-related parameters			
λM	N (191, 38.2)	N (53, 10.6)	N (333, 66.6)
k (year ⁻¹)	L (20.77, 47.16)	L (11.32, 28.58)	L (1.73, 1.90)
Kd (m ³ /kg)	N (9.9e-4, 2e-4)	N (3.8e-3, 7.6e-4)	N (3.8e-3, 7.6e-4)
Modified parameter			
ϵ	N (1, 0.2)	N (1, 0.2)	N (1, 0.2)
ϵ_1	N (1, 0.2)	N (1, 0.2)	N (1, 0.2)
Limited value	1mg/l	0.7mg/l	10mg/l

Conclusion: The first order reliability method is, in combination with analytical solutions to the transport equation, a useful method to include uncertainties in input parameters to assess pollution risk of aquifers. By this method, the failure probability of toluene, ethylbenzene and xylene (exceeding the standards of the water quality) can be quantified in space and time. Sensitivity analysis presents the importance of almost all parameters influence groundwater flowing and identifies the main sources of uncertainty. Application of risk maps will make the uncertainty as explicitly as possible for the decision-makers.