

Esko Rossi

An Index Method for  
Environmental Risk Assessment  
in Wood Processing Industry

UNIVERSITY OF JYVÄSKYLÄ

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Academic Dissertation

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## **AN INDEX METHOD FOR ENVIRONMENTAL RISK ASSESSMENT IN WOOD PROCESSING INDUSTRY**

**Esko Rossi**

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In the present study, a semiquantitative ranking method for plant-level assessments of environmental risks in wood processing industry was developed and tested. The method can be used in ranking defined processes or equipment in relation to their potential of causing adverse environmental effects. The method comprises submodels for estimating the probability of accidental hazardous material release, the expected quantity of a release, its dispersion in air, surface water or groundwater, and damage functions for calculating the environmental damages. The submodels are compositely linked allowing each submodel to be replaced as the state of the art advances.

The method was tested in a wood processing combine where 34 process units were analyzed, and the result's sensitivity to changes in input parameters as well as the method of aggregating the results was tested. The reliability of the results was examined by comparing the calculated results with critical incidents data collected from the analyzed units and with data on hazardous materials spills to surface or groundwaters reported by the Finnish wood processing industry.

The results of the study demonstrated that this new method is applicable to practical risk analyses in wood processing and related industry. The ranking order of the process units supplemented with the additional data collected during the assessment serves as a rational basis for decision making pertaining to environmental risk management programmes in industry. A major drawback in the practical application of the model proved to be the insufficient ecological information available on the parameters that describe the dynamics of processes governing both the behaviour and effects of the materials handled.

**Key words:** Environmental risks; risk assessment; index methods; accidental releases; wood processing industry.

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## **1. Introduction**

### **1.1. Background**

The concern for accidental releases of hazardous chemicals or gradual long-term impairment of the environment has increased substantially in recent years. The significance of accidental pollution events has increased now that the normal emission level has decreased as a result of more stringent environmental regulations on the one hand, and technical advancements in production and emission control processes on the other. By 1990, some 30 Finnish pulp and paper mills had biological wastewater treatment plants in operation or under construction (National Board of Waters and the Environment 1990). Recently the water courts in Finland have requested some pulp and paper companies to carry out an environmental risk analysis as a condition for a wastewater discharge permit, but the content of such an analysis has not been defined as yet.

The concept of an environmental risk analysis has been defined in a number of ways, depending on the context. In this study the term refers to a systematic examination of the structure and functions of a system and its environment in order to assess the probability and magnitude of the adverse changes the system poses to the environment. The concept of the environment is here defined to include human beings as well as the non-human biota and natural resources. Cuddeback (1989) has discussed the differences between the concepts of environmental liability assessment, audit and risk analysis. While a liability assessment deals with retrospective reviews of past operations to determine the legacy of contamination and an audit with present operations to determine the compliance with regulatory standards, risk analysis focuses on the potential environmental problems of future operations.

According to the above definition, environmental risk analysis partially overlaps with safety analysis which also includes an environmental dimension (Cassidy 1989), and the prominence of environmental aspects is increasing in safety analysis (Davies 1989).

A basic difference between safety and environmental risk analyses is that the latter considers also long-term impacts. The concept of environmental risk in general is discussed by Kylä-Harakka-Ruonala (1989), and the relations between safety analysis and environmental risk analysis by van Deelen (1989).

The term hazard refers to the inherent potential of a chemical, physical or biological agent to cause adverse effects (e.g. Suokas 1985, Falco & Moraski 1989a). A hazard in itself is not a risk but in conjunction with a probability of occurrence.

Environmental risk assessments have originally concentrated on compound specific evaluations in the development of regulatory standards (e.g. Stern 1986, Falco & Moraski 1989a) or estimates of the probability of adverse changes in the environment as a result of human activities (e.g. Whyte & Burton 1980, Barnthouse et al. 1982). Recently the majority of environmental risk assessments have been related to hazardous waste or contaminated soil sites, and a wide variety of methods have been developed for these purposes (e.g. VROM 1983, Parkhurst 1984, Rodricks 1984, Budd 1986, Haus & Wolfinger 1986, Scott 1987, Federal Register 1988, Krischok 1988, Montague & Holton 1988, Hertzman et al. 1989). Most of the methods treat only human health risks, and even if ecological risks are evaluated, they only have a minor weight in the final results. In the Soviet Union, evaluations of ecological risk mitigation possibilities are included in ecological statements which are obligatory for many projects or operations (Soviet Environmental Protection Committee 1990).

Publications concerning environmental risk assessments of industrial or commercial facilities are less frequent, and typically only one migration pathway is evaluated in the methods presented. The treatments of the source term are quite superficial, too (e.g. Kylä-Harakka-Ruonala 1989, Reed et al. 1989, Pinter et al. 1990). On the other hand, facility centred approaches to the identification and evaluation of environmental risks on a broader basis have been found necessary in practice, but such approaches are largely based on general subjective evaluations (e.g. Murphy 1986, Ettala, M. 1988, OECD 1989, Rossi 1990).

An application of safety analysis methods in estimating of the source term has often been suggested, but practical experience has negated the straightforward use of these methods (Murphy 1986, Ettala, M. 1988). The conclusion becomes evident also when the coverage and validity of the methods is critically evaluated. The conventional HAZOP study, for example, does not effectively reveal small leakages in the system (Suokas 1985), still they can be deleterious to the environment, especially in underground systems.

## 1.2. Aims of the study

There is an obvious need for structured and readily applicable methods for facility-centred environmental risk assessments. The aim of this study is to develop a method with:

- limited data requirements to assure its applicability in practice,
- the ability to rank process units according to the level of risk they pose to the environment, including human health and non-human biological risks,
- the ability to give indications for resource allocation in environmental risk management at facility level,
- the ability to identify which factors are most essential as contributors to the risk level of a single process unit,
- a multi-pathway evaluation possibility, and
- reasonable labour requirements.

The method was tested in a pulp and paper production integrate.

## 1.3. Limits of the study

The method is intended for the evaluation of environmental risks in wood processing industry. Even though the same method with some refinements is probably applicable also to other fields, this extension is not encompassed in the present study.

The environmental impacts of wood processing industry are controlled by the government and local authorities; the impacts during normal operation have been thoroughly studied since 1962, when the Water Act was passed. Therefore, the environmental risks caused by licenced long-term pollution are excluded from this study. Although there at present are no general rules concerning major accident hazards like the EC directive 82/501 for safety reports, these dangers are known (Pipatti 1989) and have frequently been analysed using the methods of safety analysis (e.g. Koivisto & Likitalo 1990, Rouhiainen 1990, Salo 1990). That is why the assessment of major accident hazards is excluded from this study.

Any evaluation of adverse environmental changes is bound to include human perceptions of natural values, and also many measurements of ecological parameters are subject to a number of elements of uncertainty. Moreover, the quantitative calculation of accident probabilities is laborious and involves a great deal of uncertainty. Environmental risk analyses are typically extensive plant level assessments, hence the application of time-

intensive methods is limited. For these reasons, the development of a fully quantitative method is bound to remain an unattainable goal. At any rate, to a certain extent, measuring risk levels is necessary, and relative ranking appears to be the most applicable level of assessment.

## **2. Formulation of the environmental index**

### **2.1. Index methods in practice**

A number of index methods have been developed for rapid rankings of process hazards at plant level in chemical and related industry. These methods are frequently used by insurance or industrial companies for evaluations of financial risks (Ettala, J. 1989). The method used by Industry Mutual (Ettala, J. 1989), the Dow (AIChE 1987) and Mond (ICI n.d.) indices can be mentioned as examples.

The method applied by Industry Mutual gives a coarse picture of the most significant risks as well as guidelines to direct resources on insurance buying and loss prevention. The identified risks are grouped into classes according to the estimated magnitude of loss and frequency of occurrence. The numerical scores 1 - 5 are assigned to the classes and the risk is calculated by multiplying the magnitude class and frequency class scores. The estimate of frequency is based on subjective evaluations made by an analyst team.

The Dow index is a widely used method of numerically rating a chemical process unit for its loss potential. It assigns penalties and credits based on plant features. Penalties are assigned to process materials and conditions. Credits are assigned to plant safety features that can mitigate the effects of an accident. The penalties and credits are combined to derive an index that is a relative ranking of the plant risk. The Dow Index serves as a tool for selecting, designing and providing the necessary preventive and protective features for new plants. It also affords a means of auditing or evaluating operative units under existing conditions.

The Mond Index was originally a development of the Dow Index. Compared to the 3rd edition of the Dow Index, which was the original basis of the Mond Index, the main developments include (Ettala, J. 1989):

- a wider range of process and storage installations can be studied,
- a number of special process type of hazard considerations shown to

- significantly affect the hazard level can be included,
- aspects of toxicity can be included in the assessment, and
- a range of offsetting factors for good designs of plant and control/safety instrumentation systems can be included.

These risk index methods require a chemical engineer or industrial chemist familiar with the chemistry and process unit layout. In addition, support from the company's business office will be required if the evaluation includes equipment replacement and business interruption costs. Each unit evaluation can be carried out by a single analyst who has knowledge of the process.

Index methods used in environmental assessments include hazardous waste site ranking systems (e.g. Haus & Wolfinger 1986), water and air quality indices (e.g. Ott 1978), as well as scoring methods used in environmental impact assessments (e.g. Canter 1977, Hollick 1981) or in evaluating natural areas (e.g. Smith & Theberge 1987). The most extensively applied ranking method is the Hazard Ranking System (HRS) (Federal Register 1988) developed for the U.S. Environmental Protection Agency.

The HRS is a scoring system evaluating the relative threat to public health and the environment from releases or potential releases of hazardous substances from uncontrolled hazardous waste sites. The HRS's final score, a number between 0 and 100, is based on scores for four exposure pathways: ground water, surface water, air and onsite exposure. The groundwater, air and onsite pathway scores are all the products of values for three factor categories: release probability, waste characteristics and targets. The score for the surface water pathway is the product of values assigned to two factor categories: release probability and consequence of exposure. The surface water pathway includes also human exposures due to food chain contamination.

## **2.2. Theoretical basis of environmental and risk indices**

According to Ott (1978), the purpose of an environmental index is to reduce a large body of data down to its simplest form, retaining essential meaning for the questions that are being asked on the basis of that data. Through mathematical manipulation, an environmental index seeks to reduce measurements of two or more environmental variables to a single number (or a set of numbers, words or symbols) that retains meaning. Although the environmental indices which have been developed show great variety and striking differences, it is possible to construct a general mathematical framework which accommodates most existing environmental indices. The overall

process -a calculation and aggregation of subindices to form the index- can be illustrated in a flow diagram (Fig.1).

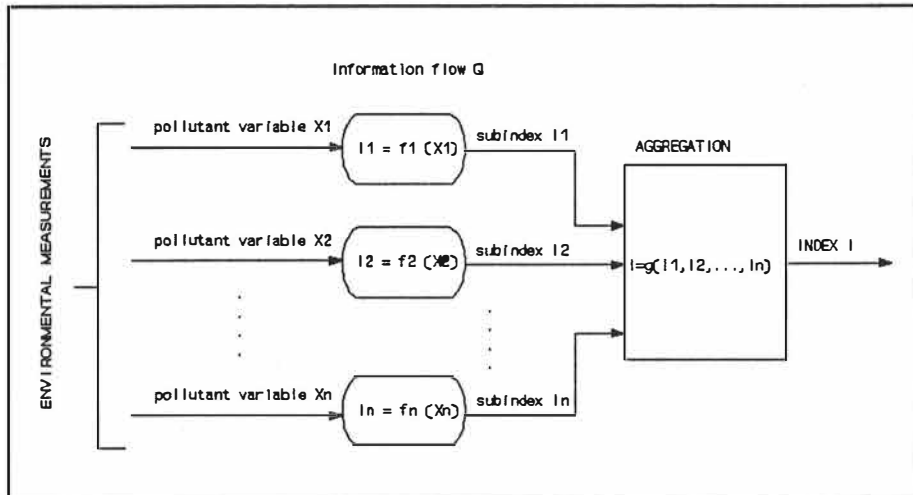


Fig. 1. Information flow process in an environmental index (Ott 1978).

The scientific basis of the index methods used is varied and a great deal of criticism has been directed to this kind of approaches that reduce the information to a scalar function (e.g. Smith & Theberge 1987, Halfon 1989). Although the principle of scoring various attributes and combining the scores to a single variate seems simple, intuitively appealing and gives a result easy to comprehend, the algorithm of the index should have a sound theoretical basis. Mathematical manipulations of the scores assigned to the variables must be in accordance with the scale of measurement. If a scoring is based on qualitative assumptions (nominal or ordinal scale), the scores should be weighted explicitly to convert them to a quantitative scale. Converting for example ordinal rankings to scores 1,2,3 etc. is improper, because the allocation of points is arbitrary and subjective. The assigning of scores should be based on a rigorous theory, e.g. mathematical models or methods of the utility theory.

Most of the common index systems use scores in the early steps of risk estimation. Thereby, rather different values of a parameter are subsummarized in one score and, on the other hand, the difference between neighbored values is overestimated when they are separated by a cut off value between two scores. For these reasons, scores should be applied at the late stages of risk estimation, or when detailed mathematical modelling is



unreasonable. An example of a step requiring modelling is the evaluation of transportation processes in environmental medias. The need to incorporate quantitative mathematical transport/fate models into the hazardous waste sites ranking system (HRS) has been recognized e.g. by the Hazard Ranking System Review Subcommittee of the Science Advisory Board (EPA 1988).

The Hazard Ranking System Review Subcommittee (EPA 1988) stressed that, to the extent possible, the result of the method should reflect the real situation in nature. To achieve this goal, the algorithm of the risk index system should rest on knowledge of the processes contributing to the risk. In practice, these systems devise detailed yet highly simplified mathematical models. Another possibility is to rely on empirical experience and develop a set of rules which can be combined and modified to match the situations in real life.

### **2.3. Functional elements of the environmental index**

The algorithm developed in this study is based on practical experience and simple quantitative mathematical models. The objective is to produce a combination which, within the limitations of resources and data, gives a feasible estimate of risk. The structure of the model consists of compositely coupled functional elements. The approach allows each element to be replaced as the state of the art advances.

The overall framework of an environmental risk assessment procedure can be derived from accident phenomena, which can in turn be divided into sequential phases. Using the investigations of accident modelling and models of accident occurrence described by several authors, Rouhiainen (1990) has presented a model illustrating the accident process and the factors which may contribute to it (Fig. 2).

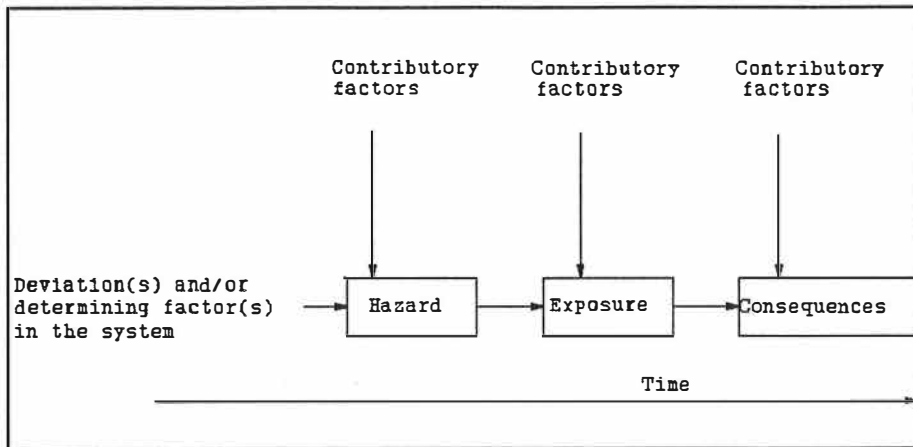


Fig. 2. A model of the accident process and the effects of contributing factors (Rouhiainen 1990).

All the phases of the accident process may be affected by two types of contributing factors: deviations and determining factors. A deviation is defined as an event or a condition in the production process conflicting with the norm for the faultless and planned process. Determining factors are relatively stable properties of the production system affecting the occurrence of a hazard. Determining factors vary only little in time and they were mainly born when the system was established.

Geyer et al. (1990) classified the causes of accidents in process industry into direct causes, origins of failure or underlying causes, and recovery failures. For example, a direct cause may be an operator opening a wrong valve, which may have had its origins in inadequate training, poor instructions or a poor identification of the valve. Furthermore, there may be found underlying causes also for the poor training, instructions or identification. Even after potential release conditions have arisen, there is often an opportunity to return the system to a safe state. A failure to recover from potential accident conditions is considered a third level accident cause.

Rowe (1975) has presented a comprehensive description of the risk determination process (Fig. 3) which covers both risk identification and risk estimation. In the context of an environmental risk analysis, the first two steps constitute the determination of the source term, and the other three steps define the environmental effects.

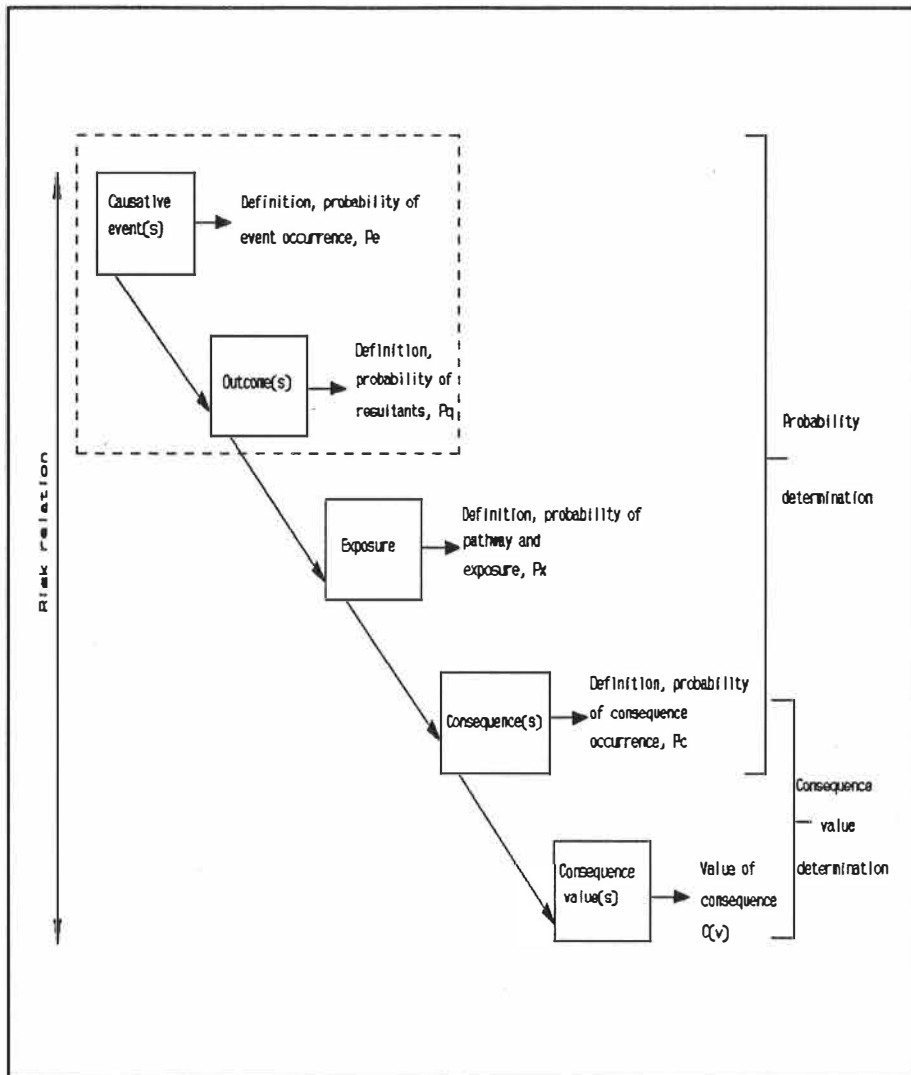


Fig.3. The general process of risk estimation (Rowe 1975).

A comprehensive environmental risk assessment procedure should take into account four factor categories for each location assessed:

- characteristics of materials,
- facility operations and practices,
- environmental routes, and
- target populations.

Material characteristics are important in every phase of the risk assessment procedure. The physical and chemical properties of a material, such as corrosivity or the physical

state, have a substantial effect on release probability. The capacity of migration off from the facility and dispersion in the environment is, in addition to technical and environmental regimes, dependent on a variety of material characteristics (e.g. viscosity, density, solubility, molecular weight, vapour pressure, degradation rates in water and soil). Finally, the biological effects on target populations are strongly correlated to the toxicity of the released material. So, the characteristics of the material can not be treated as a separate phase of the risk assessment procedure, instead they must be included in all phases. The first step in performing the index calculation is to select the material of concern.

Facility operations and practices are of ultimate importance in estimating the source term, i.e. the probability and quantity of a release. The estimation of the source term constitutes the first submodel of the environmental index. This submodel must take into account also the factors which have a substantial influence on the probability and quantity of the material migrating off from the facility after the occurrence of a discharge from the equipment.

Dispersion and dilution in the environment is an essential factor in determining the biological effects of a release. Dispersion calculations are made for surface water, groundwater and air pathways in the second submodel. Soil is not considered as a separate route, because it will be subsumed under the surface water and groundwater analyses.

Excluding soil contamination as a separate route would also mean leaving out the evaluation of damages resulting from direct contacts with contaminated soil or dust, or from contamination of terrestrial food chains, resulting from direct contacts of plants or animals with soil. It can readily be concluded, that when pulp and paper industry is concerned, the potential danger arising from direct contacts with polluted soil or polluted soil dust is relatively unimportant. Moreover, the long-term effects of persistent and bioconcentrating chemicals are estimated in a separate submodel. The most important effects of soil contamination in itself might be on a potential subsequent use of the land after the production has been brought to a halt. This effect is accounted for by estimating the decontamination costs of the release scenario considered.

The use of dispersion models in the context of highly persistent chemicals is not valid, and the hazards of chronic toxicity or biological accumulation are calculated on the basis of the amount and properties of a chemical in this model. The long-term effects assessment constitutes a separate pathway submodel independent of environmental routes. An overall calculation excludes considering the effect on target populations but was preferred for the sake of simplicity. Also the present knowledge of mechanisms and parameters especially of terrestrial food chain biotransfer factors is not sufficient for

addressing quantitative risk estimates from food chain contamination (Wang et al. 1987, McKone & Ryan 1989).

The extent of environmental damages is calculated relating the concentration and toxicity data to target populations. This relationship is called a damage function and it is an equation or a set of curves translating a predicted concentration in some element to deleterious effects on biological organisms, human health, aesthetics of man's surroundings or materials. These damages are explicitly valued and the valued magnitude of effect is referred to as the impact term of the index. One extent of target populations is the variety of effluent treatment systems, which may be damaged by certain types of spillages (e.g. toxic releases to biological wastewater treatment facilities).

The calculation of the index is the final procedure in the model. The quantity of the release and migration, dispersion and dilution calculations have been used as parameters in determining the damages to the target populations. This data must not be used again in calculating the index score. The material and pathway specific index score is calculated from the probability of a release and the valued magnitude of damages resulting from dispersion via pathway concerned. The material and pathway specific scores are summed to attain the total score for the process unit concerned.

It is a common practice in risk analyses and environmental impact assessments to assign worst-case values to parameters used in estimating the effects. Suter II et al. (1987) have argued that worst-case analyses are often unrealistic. Because there is no absolute worst case and no scale of badness, these estimates should not be used for comparing alternatives. In this study, adverse yet realistic circumstances are assumed to prevail, and a modest overestimation of the impacts is aspired.

#### **2.4. Index structure**

The index model system (Fig. 4) is composed of the functional elements described above. Each functional element includes the probability and magnitude variables, but since the environmental circumstances are roughly equal for all process units, the probability variable is estimated only for the source term.

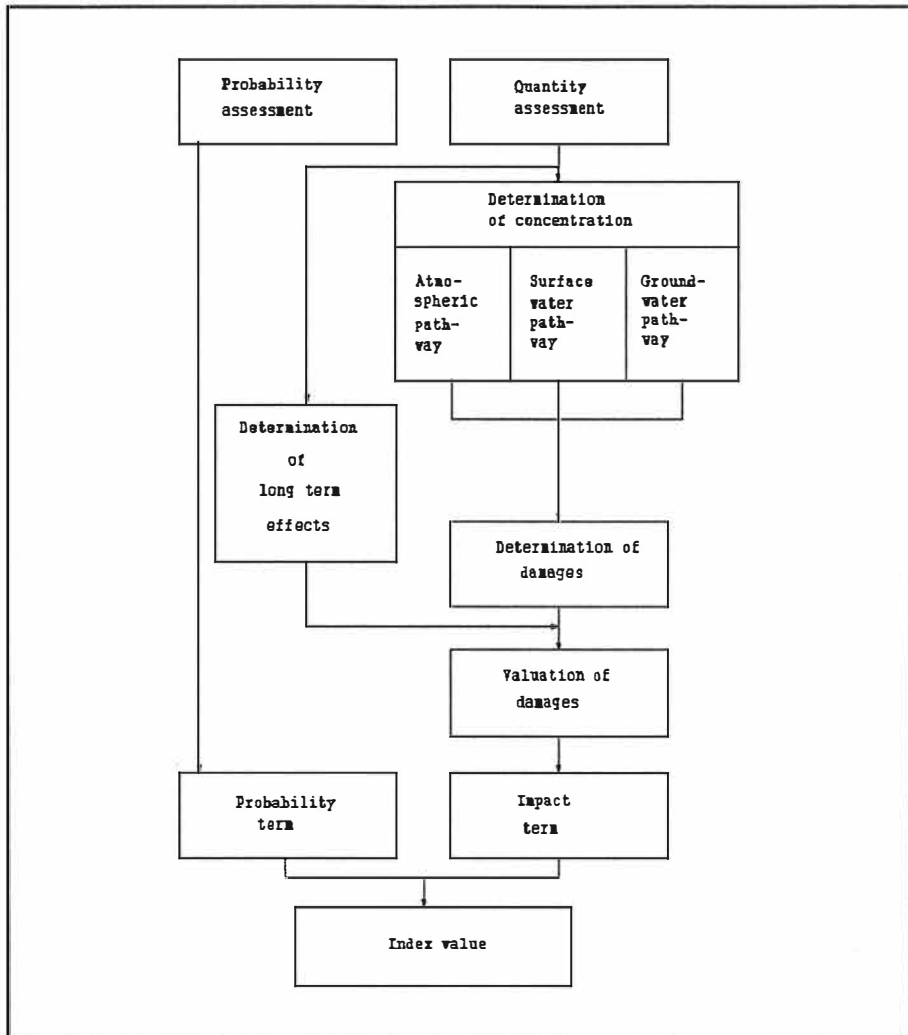


Fig.4. The overall structure of the index model.

The quantity of material migrating via a specific route is submitted to the dispersion submodel together with the information about the physical environment and defined benchmark concentrations. The dispersion submodel calculates the damaged areas or magnitude of effects within a defined area according to the benchmark concentrations. After the magnitude of effects has been determined, the damages are valued explicitly in order to transform them to comparable scores. The valuation is based on target populations in the area affected, but also other consequences of the potential damages are considered. The economic value of the damages is, when available, used to describe the effects. It is, however, transferred to a nonmonetary score to make it comparable with unpriced damages.

## 2.5. Use of the index

It is reasonable to employ the extensive experience of safety analyses when carrying out an environmental risk analysis. When a whole site is in question, it should be divided into units which in turn are split into systems to be analyzed (e.g. Kayes 1985). Every safety analysis begins by a definition and description of the system (Suokas 1985), and a system definition is essential also in the case of an environmental risk analysis.

The next phase is an identification of hazards, including an identification of factors which may contribute to accidents. In the context of an environmental risk analysis, this is equivalent to an inventory of hazardous materials. The third phase in the safety analysis is a modelling of accidents, which is followed by a preliminary evaluation and a subjective prioritization of accident risks. A facility centred environmental risk analysis is usually halted at this stage (cf. Murphy 1986, Ettala, M. 1988, OECD 1989).

The safety analysis is then continued by estimating the accident frequencies using component failure and human error data, and by estimating the consequences of potential accidents. These assessments constitute the estimation of risk. In the case of process industries, estimating the consequences of risk means the use of gas release and dispersion models, fire and explosion models, meteorological and toxicity data, to produce effect distance contours. The distance contour data is converted to a quantitative estimate of risk applying data on the number of people and value of property exposed (Kayes 1985, Kakko 1990). The decision concerning the level at which the safety analysis is stopped is based on the complexity of the analysis object and the risk potential.

When an environmental risk analysis is carried out using the environmental index, the site is at first divided into departments (e.g. digesting, chemical recovery, material storage) and a qualitative risk assessment is made at this level (Fig.5). The probability of releases is estimated by a subjective scoring. The quantity and migration pathway of a potential release is estimated roughly.

The departments are further divided into pertinent process units and index calculations are made for units whose risk level has been evaluated high or moderately high in the previous phase of the analysis. The release probability and quantity is assessed in expert meetings according to the guidelines presented in the User's Manual (Rossi 1991). The concentration and material characteristic related environmental losses are calculated and the impact term of the risk index is derived by summing the values of single loss estimates.

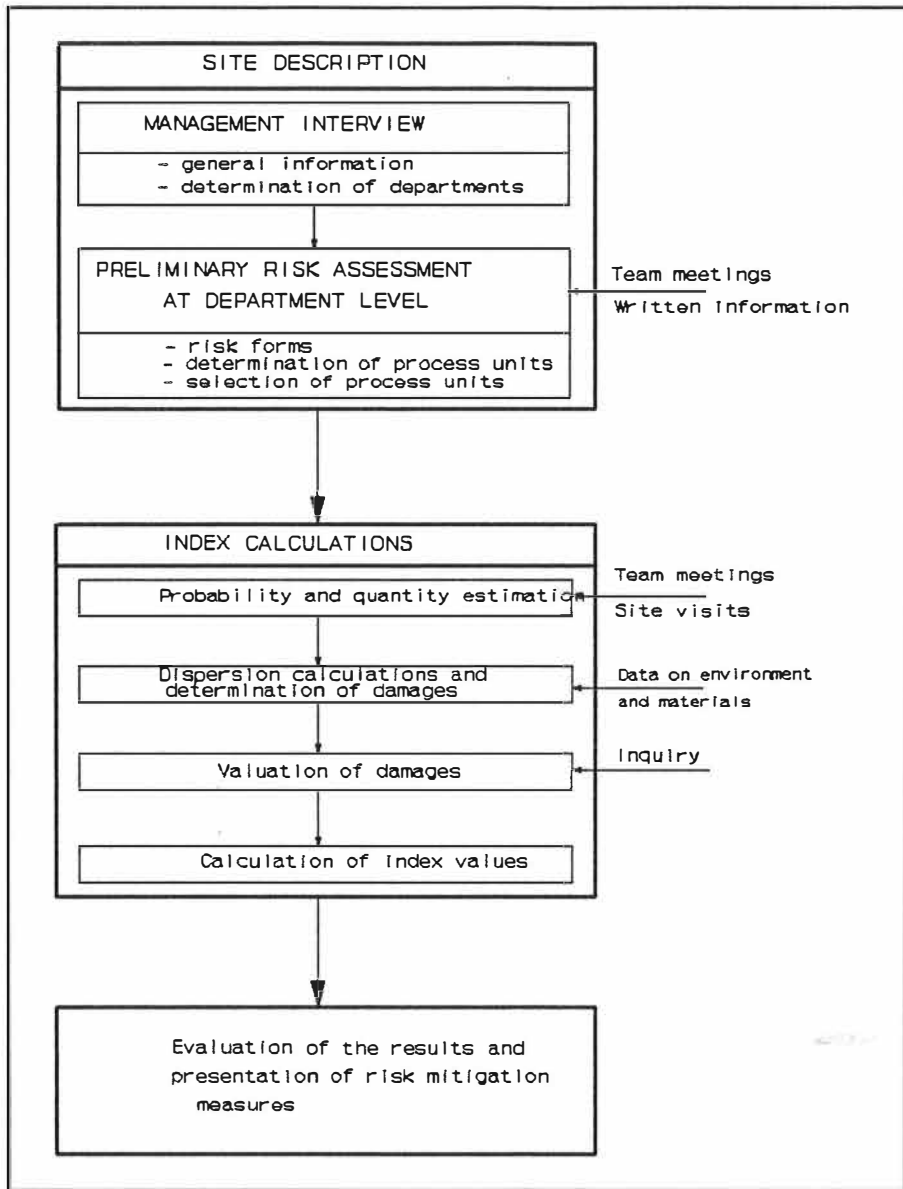


Fig. 5. The process of an environmental risk analysis using the environmental index.



### **3. Development of functional elements**

#### **3.1. Release term**

##### **3.1.1. Theoretical considerations of the release term**

The release term is defined as a descriptor of probability and quantity of releases with a potential of causing deleterious environmental effects. In this index system, the probability term stands for the probability of a material discharge from the equipment. In reference to the general risk determination process described by Rowe (1975), the probability term represents the probability of the occurrence of causative events times the probability of outcomes. The causative events are in this context failures or disturbances leading to a discharge of a hazardous material from the equipment. The occurrence of a discharge does not necessarily lead to a release to the environmental compartments, because minor discharges may be totally caught by the measures affecting the release quantities. A protective measure is included in the probability term, if it functions in binary fashion, i.e. when successful, the spill is totally caught, but when failing, its effect can be considered insignificant.

Even as regards a single process unit, there is an infinite number of discharge possibilities in the continuum from small to large discharges. Amson (1982) referred data from recorded chemical spills in the United States and concluded that the frequency of spills of various sizes is roughly lognormal. However, the experience of the author of this study suggests that the distribution of discharge sizes is more likely to be exponential. Because small size spills are not always recorded, the statistical data may give a somewhat distorted picture. Also Guymer et al. (1987) calculated a very sharp decline of probability as a function of the release volume for unloading tank trucks with high vapour pressure toxic liquid. The relationship between different scales of accidents has also been recognized in cases of fatal, lost-time, minor and non-injury accidents (Kletz 1985).

Although a relationship of some kind between accident scale and frequency is evident, the shape of the distribution is variable.

As the probability distribution of various discharge sizes is continuous, the discretization of the distribution is required for the practical assessment of the probability. The discretization can be carried out at various levels of accuracy, ranging from numerous extremely small classes (numerical integration) to rough estimations by one or two classes. A division into two classes is considered sufficient for the ranking. A more accurate estimation is not attempted, because there is not enough data to establish a fixed distribution. Furthermore, a collection of data for the distribution assessment of each process unit is not reasonable, because a plant-level semiquantitative ranking method is aspired. The two classes are:

- frequent minor discharges with insignificant environmental impacts, and
- less frequent discharges with a potential of adverse environmental impacts.

The derivation of the probability term is based on the following assumptions:

- discharges have, in respect of quantity, an approximately exponential distribution, that is to say small discharges constitute the major part of all discharges,
- the quantity of a discharge has a finite maximum, and
- the insignificant small discharges are not included in the discharge probability.

Due to the above assumptions, the probability density function of all discharges is truncated at the maximum quantity and can be described as (Bury 1975):

$$f(m) = \frac{f(g)}{1 - \int_0^{M_{\max}} f(g)dg} \quad (1)$$

The probability of discharges considered in this study can be expressed as:

$$P = p_0 \cdot \int_{mm}^{M_{\max}} f(m)dm = p_0 \cdot \int_{mm}^{M_{\max}} \left\{ \frac{f(g)}{1 - \int_0^{M_{\max}} f(g)dg} \right\} dg \quad (2)$$

where

$P$  = yearly probability of a discharge with a volume large enough to potentially cause adverse environmental impacts (= probability term)

$p_0$  = yearly probability of occurrence of a discharge.

When an exponential probability density function is assumed, the probability term is (Fig. 6):

$$P = p_e \cdot P(m > mm) = p_e \cdot (1 - F(mm)) = \frac{(e^{-\lambda mm} - e^{-\lambda M_{max}})}{(1 - e^{-\lambda M_{max}})} \quad (3)$$

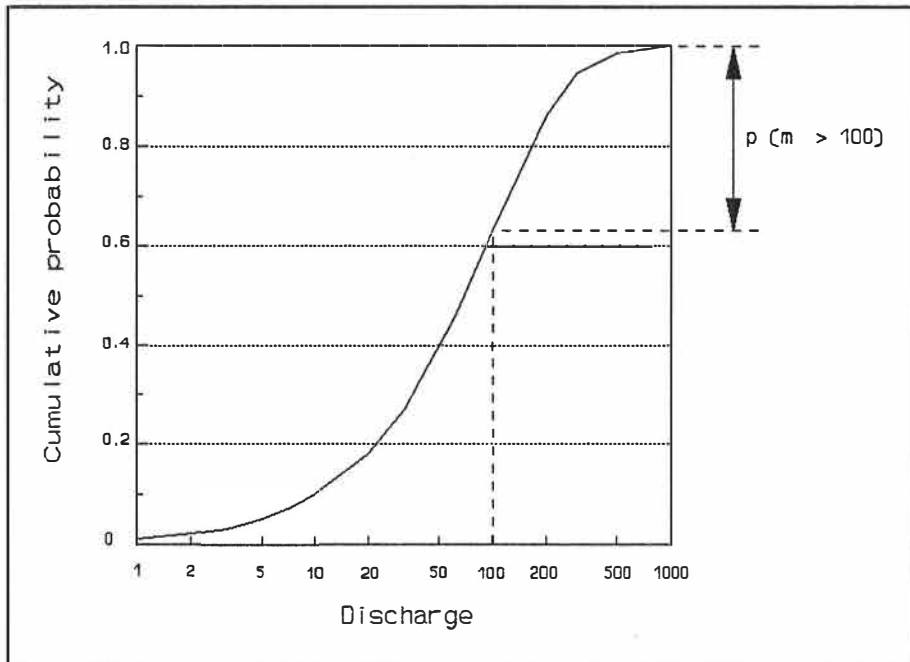


Fig. 6. A visual description of the theoretical determination of the probability term (in this example a truncated exponential with  $\lambda = 0.01$ ,  $M_{max} = 1\,000$ ,  $mm = 100$ ).

The methodology used for predicting event probabilities in quantitative risk analyses is called the probabilistic risk analysis (PRA). The traditional methodology was developed in the aerospace sector to predict risks in systems for which no operating experience is available. The probabilistic risk analysis has later been adopted to nuclear industry, but when more operational experience has accumulated, new risk analysis practices have been developed for the risk analysis of nuclear power plants.

Probabilistic risk analysis methods have been widely used also in chemical process industry in assessing quantitative risk estimates for major hazards (Guymer et al. 1987). In process industry, processes and operation conditions are more varied than in nuclear

power plants, and reliable component specific failure rate data is scarce. In addition, the level of process automation and instrumentation is lower, which makes the risks in process industry more operator-centred than in nuclear power plants. Therefore, probabilistic risk estimation of hazardous materials releases in process industry is especially difficult and the uncertainty of the results tends to be high.

When a set of similar objects is studied, the number of possible discharge scenarios is limited and they can be worked out into a fault tree. Van Deelen (1986) defined the release scenarios for underground tanks and prepared a fault tree for calculating the outflow probabilities. Cooke & Goossens (1990) have suggested applying a method called the Accident Sequence Precursor (ASP) methodology when assessing risks in process industry.

The ASP methodology does not use fault trees, but only event trees. Although there is no mathematical distinction between fault and event trees, the modelling heuristics differ. Fault trees represent 'backward logic': they enable the probability of the top event to be expressed as a function of the probabilities of the more elementary events into which the top event is decomposed. Event trees represent 'forward logic': they encode the possible responses of a plant's safety functions to an initiating event. In the ASP method, the probabilities at the event tree nodes are derived from operational data. The ASP method represents a coarser plant modelling but includes a more intensified incident data collection than the traditional probabilistic risk analysis.

Neither the PRA nor the ASP methodology is suitable for a screening system because they are too laborious. Anyway, the logic of the ASP methodology serves as a rewarding guideline for the development of a new scoring system. Because the site specific data collection should be achieved with minimal efforts, no detailed incident frequency data is to be used. Although the system is composed of general probabilities, the site specific conditions are taken into account in assigning weights to factors describing discharge probabilities.

The scoring of the probability term is based on the assumption that those features of the system which affect the probability of a discharge can be defined separately and with universal applicability. These features are divided into three classes (cf. AICHE 1987, ICI n.d.):

- general penalty factors (cf. determining factors),
- special penalty factors (cf. deviations), and
- credit factors diminishing the probability accounted by the general and special penalty factors.

Every single general and special factor represents a certain probability of a release, depending on the quality of the feature. Each credit factor deletes a portion of the total

probability accounted by the general and special factors. The overall structure of the probability term can be understood as a rough overall approximation of the accident precursor methodology where general and special features are linked through or gates and credit factors through and gates (Fig. 7).

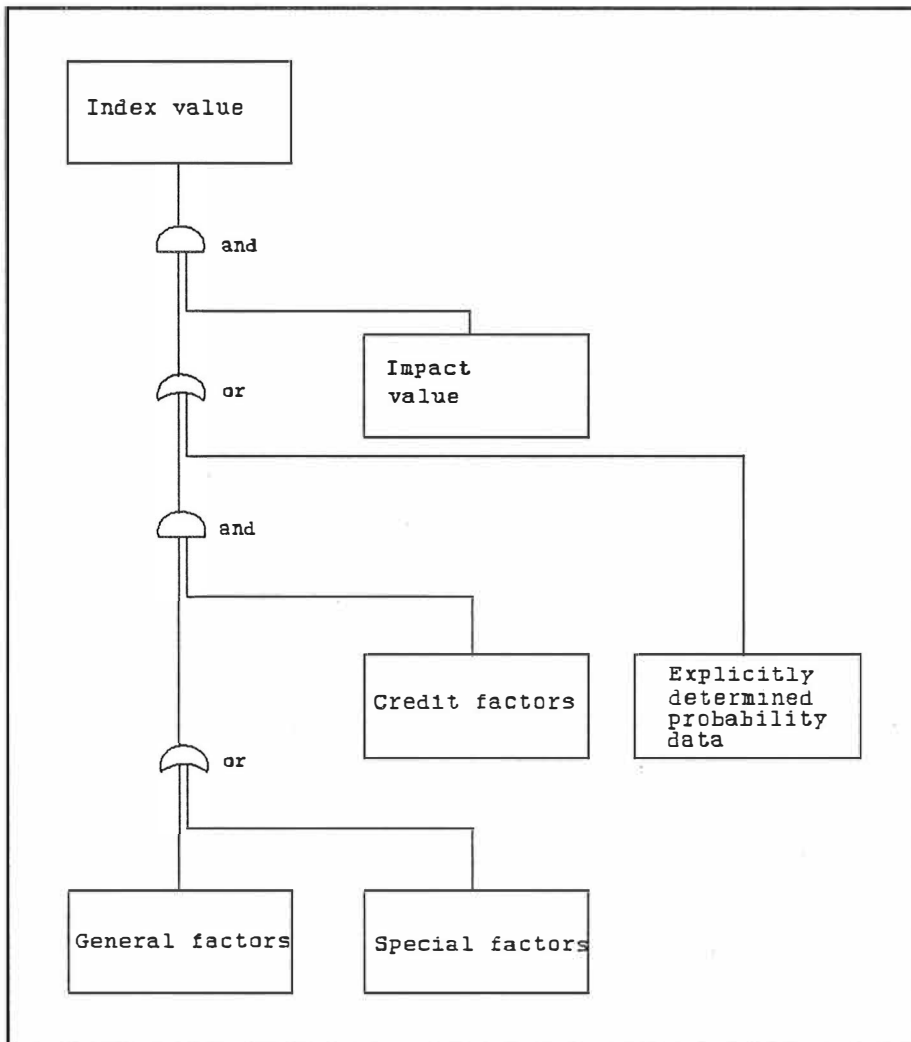


Fig. 7. The logic tree of the probability considerations in the environmental risk index.

The probability term can be expressed mathematically as follows:

$$P = (1/a)(\Sigma gf + \Sigma sf) \cdot \Pi cf \quad (4)$$

where

- P = probability term,  
 a = scaling factor,  
 gf = probability contributed by a single general penalty factor,  
 sf = probability contributed by a single special penalty factor, and  
 cf = fraction of the total probability that a single credit factor diminishes.

### 3.1.2. Development of the probability assessment system

If the probability of a discharge can be assessed reliably from e.g. statistics, such a probability value should be preferred. This is possible in the case of frequent discharges, when the factors contributing to the probability are usually known and a probability assessment using the method discussed here does not appear reasonable. Accordingly, as regards fire or explosion, the special methods and statistics are well developed and the probability of these events is presumed to be given. In general, probabilities of rare and frequent causative events are supplied explicitly and the probabilities in between are determined by means of a scoring method.

The scoring method is based on a description of an accident phenomenon and a classification of its causes. General penalty factors describe the system overall features which introduce the containment equipments necessary for an accident potential. Special penalty factors, then, represent mainly the underlying causes which may contribute to deviations to the system functioning. And credit factors account for system features with a potential to prevent the propagation of direct or underlying causes or, on the other hand, to increase the recovery potential.

Seven general and seven special penalty factors and seventeen credit factors were defined for the scoring system. The main emphasis was on factors with a realistic probability of modifications. For example, the extent of the process unit is precluded, because there are seldom realistic possibilities to modifications of that scale, except in cases of major hazards, which are beyond the scope of this study. The extent of process units can, however, be dealt with when they are confined.

Each factor consists of a set of criteria for determining the score of the factor. The weights of the factors are inherent in the scoring rules; no explicit weights are added.

These scoring rules were developed through an iterative process (Fig. 8). The first set of rules was composed by combining and modifying rules from the Dow and Mond indices. In the next phase, additional literature (Katz 1982, van Deelen 1986, Kemikontoret 1986, Palmisano & Margolis 1987, Pipatti & Lautkaski 1987, Bernath 1988, Heinold et al. 1988, Ettala, J. 1989, Geyer et al. 1990, Toola et al. 1990) and unpublished confidential data from industry were used to refine the scoring rules. Finally, desk simulations based on data from practical experience with environmental risk analyses were carried out.

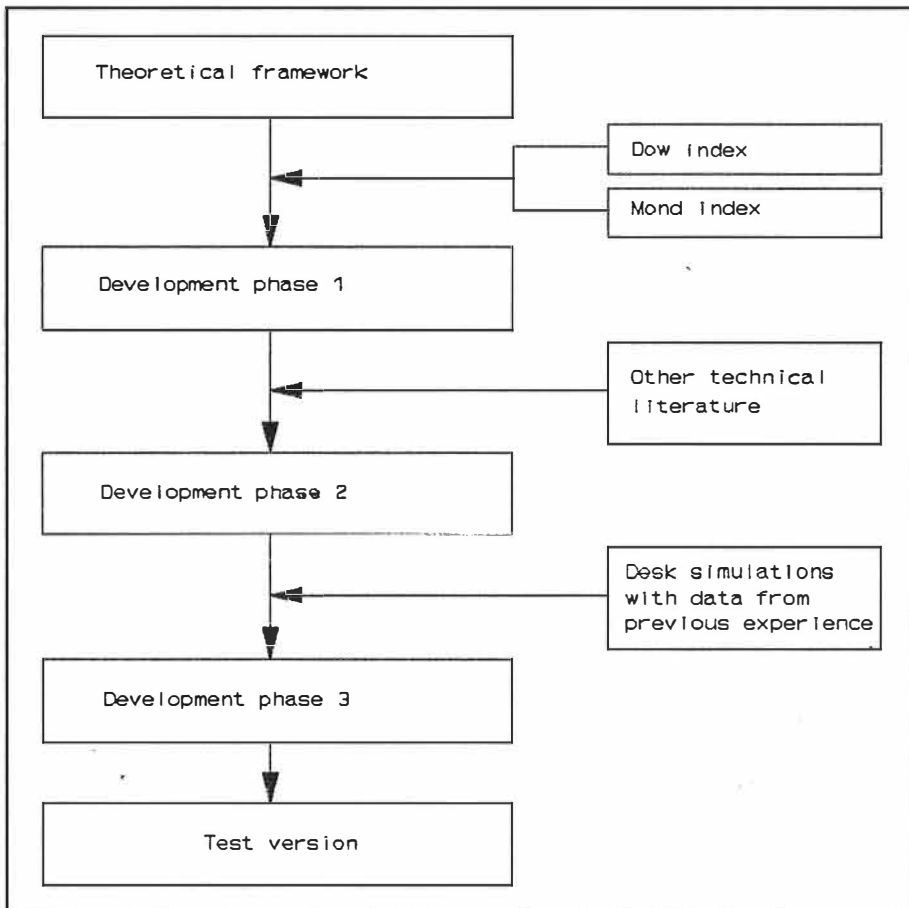


Fig. 8. The probability term generation process.

Detailed guidelines for assigning the scores are given in the User's Manual (Rossi 1991). The factors in conjunction with the contribution of each factor score to the total maximum score are presented in Tables 1 and 2.

Table 1. The penalty factors of the probability term.  
 (The minimum score of the general and special factors is 0 if the factor is non-existent)

Factor name	Range	% of max.
<u>General factors</u>		
material storage and physical processing	0.0 - 0.5	3.9
single continuous reactions or extract phases	0.2 - 1.5	11.6
single batch reactions or extract phases	0.1 - 0.6	4.6
multiplicity of reactions with the same equipment or subsequent processes	0.0 - 1.0	7.8
material transfer	0.1 - 0.8	6.2
transportable containers	0.4 - 1.0	7.8
washings and other emptyings	0.0 - 0.3	2.3
Total	0.0 - 5.7	44.2
<u>Special factors</u>		
low temperature	0.0 - 1.0	7.8
high temperature	0.0 - 0.3	2.3
temperature fluctuations	0.0 - 0.3	2.3
corrosion and erosion	0.0 - 1.5	11.6
joints and gaskets	0.0 - 0.6	4.6
fatigue, vibration, foundations and support systems	0.0 - 0.5	3.9
processes or reactions difficult to control	0.0 - 3.0	23.3
Total	0.0 - 7.2	55.8



Table 2. The credit factors of the probability term.

Credit factor	Range	% of total max.credit
Pressure vessels	0.80 - 1.00	5.8
Nonpressure vessels	0.90 - 1.00	2.9
Transfer pipelines	0.60 - 1.00	11.5
Safety basins, walls etc.	0.45 - 1.00	15.9
Spill detection and response systems	0.80 - 1.00	5.8
Recovery tanks or basins	0.45 - 1.00	15.9
Process alarm systems	0.90 - 1.00	2.9
Emergency power	0.90 - 1.00	2.9
Release risk study activities	0.70 - 1.00	8.6
Emergency shut down	0.75 - 1.00	7.2
Computer control	0.85 - 1.00	4.3
Operating instructions	0.88 - 1.00	3.4
Plant supervision	0.95 - 1.00	1.4
Management attitude	0.90 - 1.00	2.9
Environmental protection organization	0.90 - 1.00	2.9
Training in pollution control	0.85 - 1.00	4.3
Environmental protection in maintenance operations	0.95 - 1.00	1.4
Total	0.01 - 1.00	100.0

The scaling factor  $1/8$  is used to reduce the total score value to represent the annual probability of an event's occurrence. It must be stated that in spite of considerable efforts to consistency and representativity, the probability term contains subjective evaluations to a noticeable degree. No attempts at totally eliminating subjectivity were made, because a purely objective process is likely to give a restricted and therefore incomplete rating that would quite possibly be even inaccurate. Some degree of freedom, although limited,

leaves room for creativity which is no doubt necessary, since system features can never be identical.

### 3.1.3. Quantity assessment

As described in the previous chapter, the quantity of a discharge is in itself a random variate. The probability term was defined as the probability of discharges with a quantity between  $m - M$ . The quantity term is in theory the expectation value of this quantity range. In practice, the value is obtained through heuristical evaluations.

In the case of batch processes or material storage, the quantity term estimate is based on the total material quantity stored in containers and equipment at the time of a disturbance. The estimate for continuous processes is derived from the material flow in the main transfer system of the process unit. The entire quantity of the material escaped from the equipment very rarely migrates to the environment, because some proportion of the spill is retained within the facility.

The factors restricting the quantity of material migrating from the equipment to the environment consist of a probability and a magnitude component, and the shape of the distribution is variable. The joint distribution cannot be solved analytically, and, for practical reasons, the quantity diminishing factors are supposed to function at their expectation value of capacity. Like the discharged quantity, the expected capacity must be evaluated heuristically.

The assessment of the quantity term begins with an identification of possible release cases. Then the outflow rate is calculated using technical data of the equipment and equations fitting to the particular case to be calculated. There are well known simple equations for most cases encountered in practice. Kayes (1985) has presented a set of these equations together with instructions for determining the size of a rupture hole.

In most cases, the time of outflow is required for calculating the quantity of discharged material. The maximum time that an outflow might last is judged using information on control practices (e.g. instruments, time interval between inspections) and the measures required to stop or slow down an outflow. The minimum, average and maximum times of outflow and corresponding spill quantities are estimated.

To calculate the amount of material discharged to each migration route, two sets of response measures are specified as flow blockages and response capability.

Flow blockages include catch basins, shut valves, diking etc, while response capability consists of the measures to retain a spill or a proportion of it within the installation.

Response capability comprises such elements as the availability of spill recovery containers, pumps or absorbents and their accessibility to the personnel.

After the quantity of a discharge to each migration route has been estimated, the possible migration routes are checked and their treatment capacities are evaluated. The migration routes examined are:

- wastewater works,
- rainwater works,
- flooding,
- infiltration into the ground, and
- ventilation.

The treatment capacity of wastewater or rainwater works includes oil separators, strippers and wastewater treatment facilities. In the case of ventilation, the purifying equipment, e.g. scrubbers and flares, are included. Detailed instructions for the assessment of the quantity term are presented in the User's Manual (Rossi 1991). After each migration route is evaluated, the magnitude of the release to each environmental pathway can be presented for further use in dispersion models (Fig. 9).

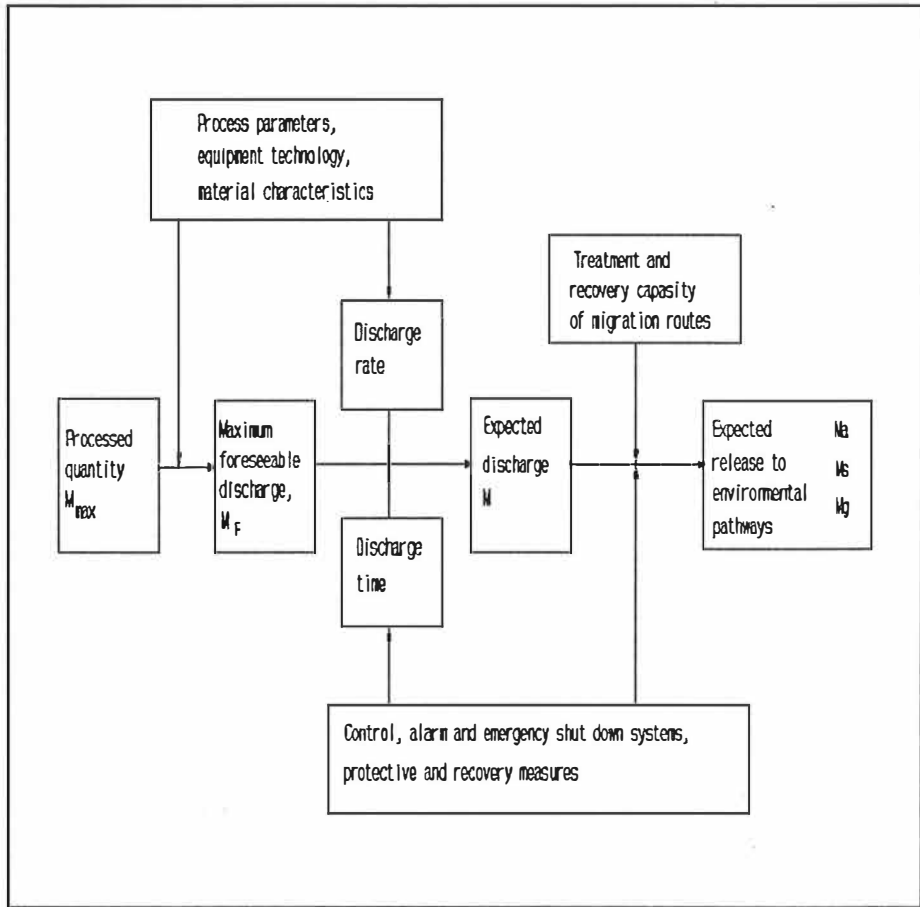


Fig. 9. The procedure of a release quantity assessment.

The so-called domino effect is evident with fires and explosions, and the discharge quantity is calculated supposing that the total quantity of material in the equipment within the possible damage area has escaped. The measures diminishing the amount of material migrating to the environmental pathways are evaluated using the same approach as presented for non-fire or explosion discharges.

## 3.2. Dispersion term

### 3.2.1. Dispersion in the air

Airborne toxic chemical releases are the most important accident scenarios in safety analyses concerning major accidents. Because of the limited scope of this study, the treatment of airborne releases is not extensive. In this context, the objective of calculating the impacts of airborne releases is to give a relative ranking of the process units in relation to the risk of accidental toxic gas emissions imposing danger to people nearby. For chemicals that are inherently toxic, the hazard zone depends primarily on the following factors: material release quantity, prevailing atmospheric conditions, limiting concentration, source geometry, surrounding terrain and density difference. The research conducted on these topics is extensive (e.g. Kakko 1990); in the present study it is not possible to discuss these topics in detail.

It is assumed that atmospheric conditions do not differ so much between the various application sites as to have any significant effect on the relative impacts. Therefore, the meteorological conditions except for wind direction are excluded from this index. The probability distribution of wind directions is taken into account in evaluating the consequences of airborne releases. Mudan (1989) has concluded that source geometry and density difference affect the near source dispersion, which is not a primary concern here. Furthermore, the omission of source geometry and density difference leads to a modest overprediction of actual hazards.

In the case of frequent releases, the assessment of a damage area is based on experiences of past releases. As for infrequent releases, simple dispersal calculations are made, based on the following assumptions (Mudan 1989):

- the release is instantaneous,
- the release source is on ground level,
- the material is neutrally buoyant, and
- the weather conditions are adverse (stable, 2 m/s wind).

The toxic hazard zone is a direct measure of the downwind dispersion distance to a specified limit concentration. As the effects studied are immediate health damages, exposure time is not considered. For the purposes of toxic gas hazard zone estimation, the chemicals are broadly divided into the following three classes:

- Class I:** Highly reactive or volatile chemicals. These are substances that vaporize very rapidly and completely and have the potential for a release to the atmosphere in a matter of moments. These include compressed gases, chemicals that may undergo exothermic runaway reactions and chemicals with normal boiling point  $< -20\text{ }^{\circ}\text{C}$ .
- Class II:** Chemicals with boiling point  $> -20\text{ }^{\circ}\text{C}$ . Here the vapour release rate is governed by the extent of boil off of the spilled liquid.
- Class III:** Chemicals with boiling point  $> 0$ . Here the release rate to the atmosphere is determined by the vapour pressure of the liquid. For chemicals with boiling points slightly below the ambient temperature, the vapour pressure is assumed to be one atmosphere.

For Class I material, which includes release of gases, flashing of highly volatile liquids as well as materials released from violently ruptured vessels, the dispersion is assumed to be similar to that of an instantaneous source. For liquids with boiling points  $> -20\text{ }^{\circ}\text{C}$ , a boiling pool is formed. The source strength, therefore, is a function of the boiling point. For liquids with boiling points  $> 0\text{ }^{\circ}\text{C}$ , the vapour pressure at pool temperature is the driving force. The pool area is based on an assumed constant thickness of about 0.013 m. The following equations are used for calculating the hazard zones (Mudan 1989):

class I chemicals:

$$S_{AH} = 9000 [ Ma / (Ca_H \cdot Mw) ]^{2/5} \quad (5)$$

class II chemicals:

$$S_{AH} = 56 [ Ma \cdot (5 - Bp) / (Ca_H \cdot Sg) ]^{3/4} \quad (6)$$

class III chemicals:

$$S_{AH} = 1.3 [ Ma \cdot Vp / (Ca_H \cdot Sg) ]^{3/4} \quad (7)$$

where

- $S_{AH}$  = downwind hazard distance (m)  
 $Ma$  = mass released to air pathway (kg)  
 $Mw$  = molecular weight

Sg	= liquid specific gravity (water = 1.0)
Bp	= boiling point (°C)
Vp	= vapour pressure (mm Hg)
Ca <sub>H</sub>	= limiting concentration (ppm)

A special case arises for Class II and Class III chemicals when the limiting concentration is very low and the predicted toxic hazard zones are very large. The chemical may evaporate relatively rapidly in comparison with the time to travel the distance. Therefore, the assumption of continuous boiling or evaporation is no longer valid. Hence, computation of "Flag" is required for Classes II and III chemicals:

$$\text{Flag} = 6 \cdot 10^8 [\text{Ma} / (\text{Mw} \cdot \text{Ca}_H \cdot \text{S}_{AH}^{7/3})] \quad (8)$$

If the numerical value of "Flag" is greater than unity, no further corrections are necessary. If the value is less than unity, the S<sub>AH</sub> computation is revised with the equation given for Class I chemicals.

### 3.2.2. Dispersion in surface water

In the migration to surface waters, two principal routes with substantial differences in the consequences of the release can be defined: a route with a wastewater treatment facility and a route without one. In addition to this fundamental division, there may be other slighter differences between the routes, e.g. in relation to physical or chemical pretreatment devices. These devices are taken into account in the assessment of the release quantity. Furthermore, the recipient may be river, lake or sea. The surface waters dispersion model consists of four submodels (Fig. 10).

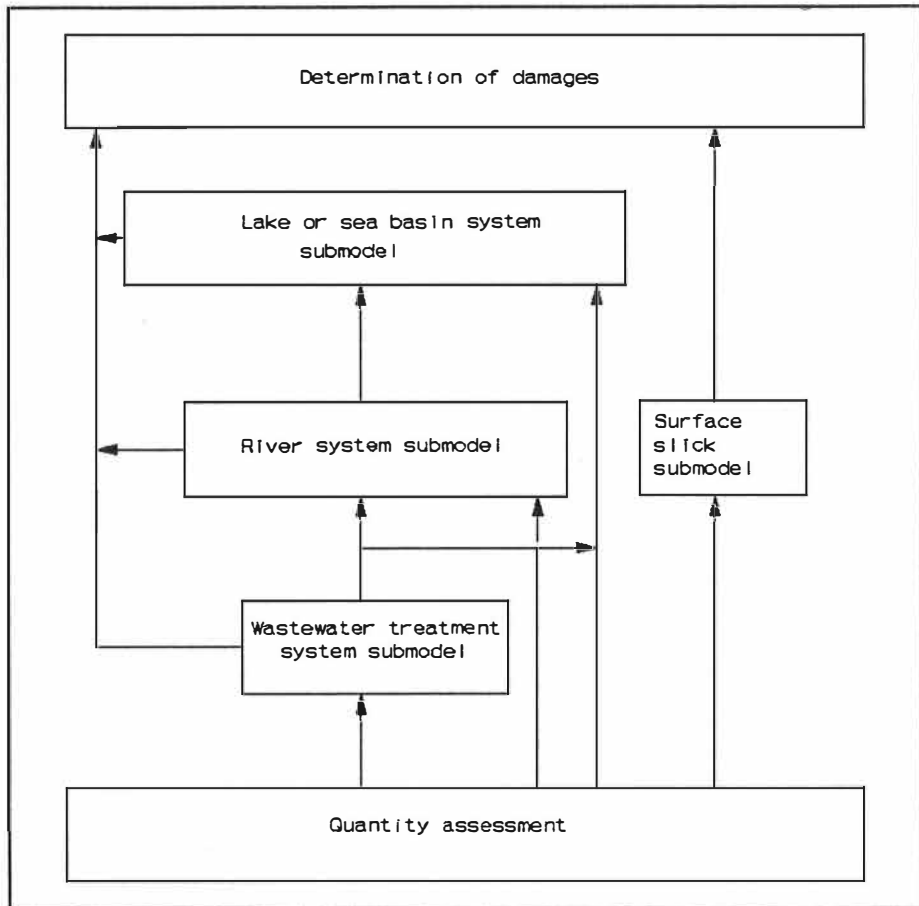


Fig. 10. The main components of the surface waters dispersion model.

Activated sludge treatment is the most frequently applied wastewater purification method in the Finnish pulp and paper industry. A typical facility consists of primary clarification basin(s), aeration basin(s) and secondary clarifying basin(s) (Fig. 11). Quite often an activated sludge facility is also furnished with an equalization basin and an emergency basin where the wastewater can be directed in the case of a detrimental release. Though not considered here, the function of the emergency basin can be taken into account in the probability term of the index.

Because it is the aeration basin(s) where the concentration of a released deleterious material is of interest, also the secondary clarification basins can be omitted if pass-through effects are not considered. The model does not account for sludge recirculation, which speed up mixing the released material from aeration basin to secondary clarifier. Therefore, omitting the effect of sludge recirculation leads to a modest overestimation of aeration basin concentration. Only the highest concentration in



each aeration basin is recorded. This dilution calculation procedure is valid also for most other wastewater treatment systems.

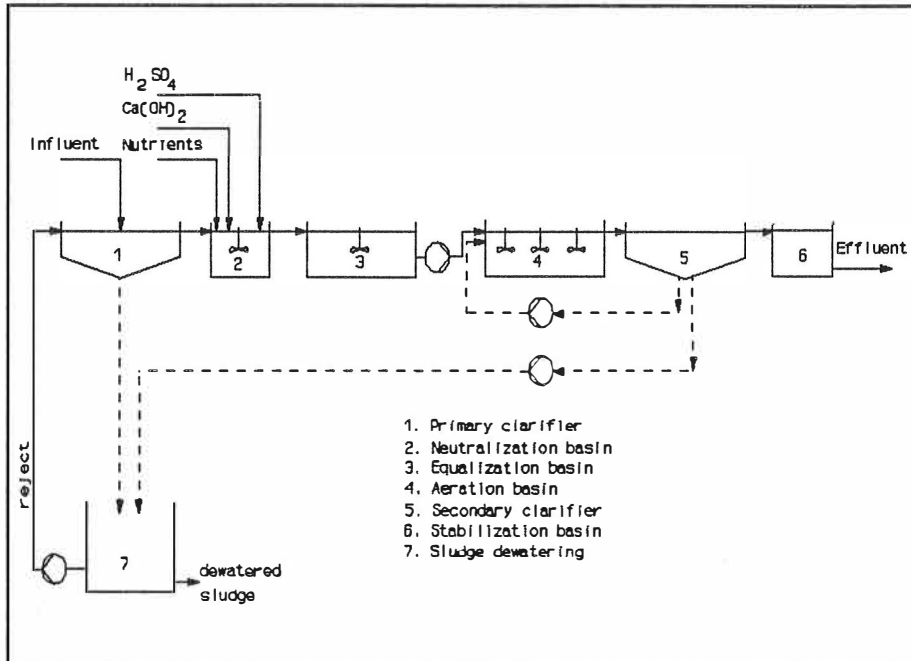


Fig. 11. A schematic description of an activated sludge treatment facility used in dilution calculations.

The single basin dilution of an activated sludge treatment facility is calculated using the equation:

$$C_i = \max \{c_{ik}\} \quad (9)$$

$$c_{ik} = c_{ik-1} + [(c_{ik} - c_{ik-1})](Q_w/V_i)\Delta t \quad (10)$$

where

- $C_i$  = maximum concentration in basin  $i$  (mg/l)  
 $c_{ik}$  = concentration in basin  $i$  at time  $k \cdot t$  (mg/l)  
 $c_{ik}$  = influent concentration to basin  $i$  at time  $k \cdot \Delta t$  (mg/l)  
 $Q_w$  = wastewater flow ( $m^3/h$ )

- $V_i$  = effective volume of a basin  $i$  ( $m^3$ )  
 $\Delta t$  = time step (h)

The effluent concentration in a basin at any step is used as influent concentration in following basin. The iteration is continued until the concentration in the critical basin has passed its maximum. As was described above, the effects on a wastewater treatment plant are calculated from contaminant concentration with no reservation on substrate concentration. Volskay & Grady (1988) have presented that this approach is valid when the inhibitor behaves in a noncompetitive way. Because of the scarcity of data, noncompetitive behaviour is generally accepted in this model.

Transport and dispersion of a release in a river system has often been approximated using a one-dimensional equation (van Genuchten 1981):

$$\partial c / \partial t = D_L (\partial^2 c / \partial x^2) - u (\partial c / \partial x) + S \quad (11)$$

where

- $x$  = distance in direction  $x$   
 $D_L$  = longitudinal dispersion coefficient  
 $u$  = flow velocity in direction  $x$   
 $S$  = concentration rate of change caused by nonhydraulic physical, chemical and biological processes.

Hypothetical applications of this one-dimensional river model have been described by e.g. Kontaxis & Nusser (1982) and Kylä-Harakka-Ruonala (1989).

A short-duration release causes a time-variable distribution of concentration at different points of a waterway. The time related effective concentration to which a target population is exposed constitutes the exposure. The exposure is defined as the integral of concentration over time:

$$E = \int c(t) dt \quad (12)$$

where

- $E$  = exposure  
 $c(t)$  = time-dependent concentration.

If the effect of the exposure is presumed to be independent of the time related concentration profile, a simple practice of calculating an average concentration could be applied when determining the effects. French & French (1989) have analyzed a large volume of test data and demonstrated that the use of an average concentration is not valid. In order to simplify the calculations, only the maximum values of spatial concentration distributions are utilized in this index system. Excluding the variability of concentration with time has no significant effect on the results within a single recipient. The differences between the recipients may be substantial if the retention time is very low in some recipient. In these cases, the error due to the concentration's steep time-dependence must be treated explicitly.

Using the equation (10) in calculating the dilution in the basins of the activated sludge facility is justified, because the mixing is efficient. Although this is seldom true of a lake (or sea) basin system, the dispersion calculation for a lake basin is made using the equation (10) with slight modifications:

$$c_{ik} = c_{ik-1} + [Q_{1i} \cdot c_{i_{ik}} - (Q_{1i} + Q_{2i})c_{ik-1}] \Delta t / V_i \quad (13)$$

where

$Q_{1i}$  = contaminated inflow to basin i (m<sup>3</sup>/h)

$Q_{2i}$  = uncontaminated inflow to basin i (m<sup>3</sup>/h).

The problem of partial mixing is handled by incorporating a subjective element in the definition of the basins. The lake is divided into consequent basins and, when necessary, only a portion of the water volume is considered to involve in diluting the release. The shape and number of the basins should be in accordance with the migration and mixing of wastewaters during a normal emission situation, with the exception that the specific gravity of the accidental release may differ from that of wastewater. The iteration is continued until the concentration in the basin begins to decline. The maximum concentration in each basin is recorded.

### 3.2.3. Dispersion in groundwater

Soil and groundwater can be described as a two-phase system, in which contaminants partition between immobile solid constituents and the mobile aqueous phase. The sorption of contaminants is highly significant as regards their rate of underground transport. The rate of biotic and abiotic transformations may also be significantly altered by sorption.

These processes determine, either directly or indirectly, the rates at which contaminants applied on the ground surface migrate through the vadose zone as well as the amounts that are subsequently delivered to the saturated zone (Rao 1990). Mackay et al. (1985) have presented an overview of the transport of organic contaminants in groundwater.

A variety of modelling techniques has been used to predict the contaminant movement in groundwater (Hejde et al. 1985). Out of the environmental risk index systems reviewed in this study, the Remedial Action Priority System (RAPS) (Whelan et al. 1985) is the only one that uses analytical dispersion models for forecasting contaminant transportation underground. The use of detailed groundwater models is understandable, because RAPS is intended primarily for evaluating the risks of radioactive waste sites, and radioactive wastes undergo a steady decay process even in groundwater zones. In a comparison of various risk index models (Industry Economics Inc. 1988), the underground transportation phenomena appeared to be of minor importance in relation to the uncertainties in the assessment of a source term and environmental regimes. Furthermore, the application of detailed groundwater models to aquifers in glacial deposits is, due to their complex hydrogeological regimes, uncertain and laborious (Jaffe & DiNovo 1987).

For groundwater pollution potential calculations, release events are divided into two categories: incidental and continuous releases. In the case of incidental releases, the contaminant applied on the ground surface is assumed to migrate to the saturated zone as a separate phase or to be sorbed in the vadose zone, depending on the amount and quality of the contaminant in relation to the depth of the vadose zone and soil texture. Volatilization may be important and it should be accounted explicitly when substantial. Jury (1988) has suggested that volatilization is significant if Henry's Law constant is more than  $2.5 * 10^{-5}$ .

In the incidental spill submodel, no degradation processes are considered to exist when the contaminant migrates forward from a nonaqueous phase of plume. Degradation is excluded because the depth of the nonaqueous plume is variable and difficult to estimate. Here the contaminant concentration is assumed to be high enough to inhibit biological decay. If the depth of the nonaqueous plume can be assessed with considerable accuracy, the mass transferred from nonaqueous to aqueous phase can be used as input to the continuous release submodel. Guidelines for assessing of the nonaqueous phase behaviour are given in the User's Manual (Rossi 1991).

To calculate the amount of contaminants transferred from the nonaqueous contaminant plume to groundwater, the areas of horizontal and, in reference to groundwater flow, vertical projection of a plume, are estimated. The plume is flushed by infiltrating water in horizontal and by groundwater flow in vertical projection, which dissolve contaminants

from the plume (Fig. 12). This method gives an overestimation of the resultant concentration, if the projections and the maximum concentration have been chosen correctly. Mackay et al. (1985) have postulated that the maximum concentration in groundwater is usually an order magnitude lower than the solubility limit.

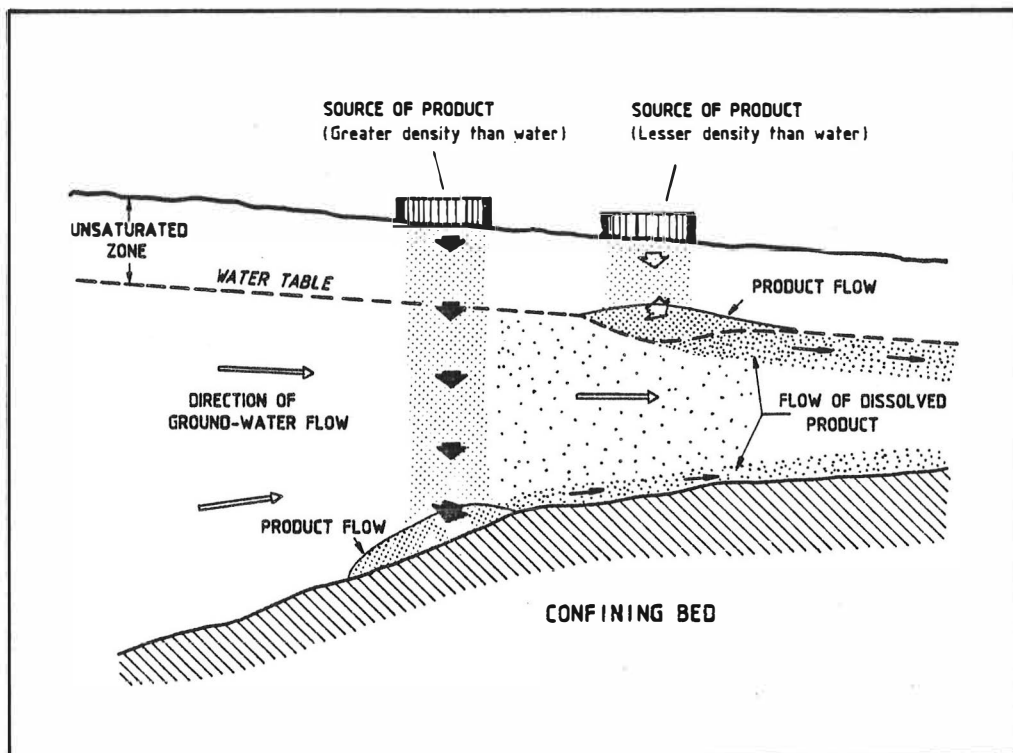


Fig. 12. A schematic representation of a lighter than water (a) and heavier than water (b) nonaqueous liquid phase plume.

The dissolved contaminants are assumed to be transported unchanged to the groundwater discharge point or, in case groundwater is utilized, to a well. For the reasons discussed above, no solute transport model is used for the saturated zone. Instead, the factors of plume migration, spread and potentially affected groundwater discharge are estimated by a qualified hydrogeologist. The assessment of aquifer parameters is of crucial importance in the concentration calculations. Instructions for assessing aquifer parameters are given in the User's Manual (Rossi 1991). The resultant concentration is calculated as follows:

$$C_{gD} = C_0 + (I \cdot A_h + v_{Gw} \cdot A_v) \cdot C_{gmax} / Q_A \quad (14)$$

$$C_{gsw} = (Q_A / Q_{Dw}) C_{gD} \quad (15)$$

where

- $C_{gD}$  = concentration in discharged groundwater (mg/l)  
 $C_0$  = background concentration (mg/l)  
 $C_{gsw}$  = concentration in groundwater discharge well (mg/l)  
 $I$  = net infiltration (m/d)  
 $A_h$  = horizontal project area of a separate phase plume (m<sup>2</sup>)  
 $v_{Gw}$  = average groundwater flow velocity (m/d)  
 $A_v$  = vertical project area of separate phase plume (m<sup>2</sup>)  
 $C_{gmax}$  = maximum dissolved concentration in groundwater in touch with plume (mg/l)  
 $Q_A$  = aquifer discharge as defined by expert (m<sup>3</sup>/d)  
 $Q_{Dw}$  = drinking water intake rate (m<sup>3</sup>/d)

If the contamination source is continuous, it is assumed that in the long run the introduced mass flux of a contaminant,  $M_g$ , will reach equilibrium with discharged (including volatilization),  $M_{g_d}$ , and degraded,  $M_{g_{deg}}$ , mass fluxes:

$$M_g - M_{g_d} - M_{g_{deg}} = 0 \quad (16)$$

Although some biological degradation in the saturated zone is evident (e.g. Borden & Bedient 1986, Borden et al. 1986), its contribution is usually minor as compared to degradation in the vadose zone. In this model, no degradation is accounted for in the saturated zone. Volatilization is included in the assessment of decay constants in the vadose zone.

In the model, the contaminant is assumed to undergo linear, reversible, equilibrium adsorption and first order biochemical decay, while moving downward through soil by leaching at a uniform average drainage rate. Deterministic models describe the vertical displacement of an undispersed plug flow in the vadose zone in a time unit (Haith & Laden 1989):

$$V_E = I/(R \cdot \theta) \quad (17)$$

where

- $V_E$  = chemical movement (m/d)  
 $R$  = retardation factor  
 $\theta$  = volumetric soil moisture content (cm<sup>3</sup>/cm<sup>3</sup>)

Using the equation (17), the time required of a contaminant to travel to depth  $Z$  can be calculated, and the mass of contaminant introduced to the surface is at depth  $Z$  (Jury et al. 1987):

$$Mg_z = Mg \cdot e^{(-k \cdot Z)/V_E} \quad (18)$$

where

- $Mg$  = mass of contaminant introduced at the surface (kg),  
 $Mg_z$  = mass of contaminant at depth  $Z$  (kg),  
 $k$  = net loss rate (1/d).

Because microbiological activity decreases with depth, the constant decay rate cannot be supposed to remain through the vadose zone. Jury et al. (1987) have suggested dividing the vadose zone into three regions:

- surface zone where the biological decay is constant,
- lower vadose zone where the microbial population density and first order decay rate decline exponentially, and
- deep vadose zone where both the microbial population density and the decay constant have residual constant values.

To avoid the problems related to defining the boundary between lower and deep vadose zones, only two regions are separated in this study. The surface zone is the biologically active layer that extends to the depth of the rooting zone ( $Z_s$ ) and has an assumedly constant decay rate. The lower vadose zone ranges to the saturated depth ( $Z_s \rightarrow Z_R$ ) and its decay rate has a constant residual value. The mass of a chemical at the boundary depth,  $Mg_s$ , is first calculated by inserting the parameter values of the upper vadose zone in equation (18) and the residual mass,  $Mg_R$ , approaching the saturated zone is derived by inserting the values of the lower vadose zone:

$$M_{GR} = M_{Gs} \cdot e^{-k_R(Z_R - Z_s)/V_E} \quad (19)$$

where

$k_R$  = decay constant in lower vadose zone (1/d)

The concentrations in question are:

$$C_{GD} = C_0 + (M_{GR} / Q_A) \cdot 1\,000 \quad (20)$$

$$C_{Gw} = C_0 + (M_{GR} / Q_{Dw}) \cdot 1\,000 \quad (21)$$

The horizontal area is not considered in the continuous case; therefore the contaminant discharge per unit area is omitted, too. If the soil texture is coarse and the contaminant is introduced to an extremely small area, it may migrate as a separate nonaqueous phase to groundwater or to the lower vadose zone. In this case, biochemical decay is limited because the residence time is short and the high contaminant concentration may inhibit biological processes. Therefore, the possibility of nonaqueous phase transport must be checked if the contamination source is concentrated. Models for predicting nonaqueous phase transport in an unsaturated zone have been presented by e.g. Pinder & Abriola (1986), Ostendorf (1990) and Reible et al. (1990).

### 3.3. Impact term

#### 3.3.1. Air dispersed releases

The impact term consists of damage functions and a valuation of damages. As regards airborne releases, only human health damages and nuisance effects are accounted for in the assessment of damage functions. Non-human biological effects are generally considered relatively unimportant in cases of short term releases. Also non-human effects can, however, be included by relating them to human health effects. The IDLH- value is chosen as the most suitable benchmark concentration for health damage evaluations and hazard zones are calculated by using the models presented in chapter 3.2.1.

The number of people exposed to a dangerous concentration of a toxic chemical depends on the following conditions:



- the area exposed to toxic concentration,
- the number and location of people within the hazard radius, and
- the variability of wind direction.

In addition, also a number of other factors such as people's ability to escape and the availability of protective devices or shelters, may be important.

The lateral area of a plume increases as the plume drifts downwind. In order to assess the true effect of instantaneous airborne releases, an analyst should examine concentration profiles as a function of time at locations of interest. Because the purpose of this model is only to give an indication of possible off-site health effects, a linear relationship between the magnitude of impacts and the radius of the hazard zone is adapted to this index system. The variability of wind direction and location of potentially exposed people as well as other contributing factors are considered when determining the reference distance where the index reaches the specific value. The damage function for airborne toxic releases is:

$$EF_{AH} = S_{AH}/Da_H \quad (22)$$

where

$EF_{AH}$  = magnitude of the health effect of airborne toxic reases

$Da_H$  = distance from the release point where the effects reach a specified value (m)

The nuisance effects are considered only for frequent releases for which the effective distance can be estimated on the basis of experience. Two zones, one heavily and the other moderately affected, are defined per each potential release scenario considered. The value of the impact term is calculated by relating these zones to the reference zones defined in conjunction with the valuation of effects. Inside the heavily affected zone, a 100 % effect, and inside the moderately affected zone, a 50 % effect is assumed.

### 3.3.2. Surface water dispersed releases

Instantaneous releases of hazardous materials into surface waters causes ecological damages and impose health risks on humans consuming water or using it for recreational purposes. If the release goes via a biological wastewater treatment plant, it may inhibit the purification process or, in extreme cases, destroy the main part of the activated sludge. If other types of wastewater treatment are used, releases of certain chemicals

may also have detrimental effects on the treatment systems.

For assessments of pollutant effects on freshwater and marine ecosystems, a variety of ecotoxicological adverse effects known as end points have been proposed (Falco & Moraski 1989b). Potential end points occur at the level of an individual organism, the population and the ecosystem. End points at lower levels of the organization have been used more widely, because they are simpler and can be assessed more rapidly and inexpensively. End points at the population or ecosystem levels are more complex and difficult to interpret, yet theoretically they appear more realistic because they incorporate the complexity of interactions among organisms and between organisms and their abiotic environment. Examples of models that describe pollutant effects at ecosystem level, are the Standard Water Column System (SWACOM) (O'Neill et al. 1983) and an ecotoxicological model described by Benz (1985).

Although the extent to which end points at lower organizational levels can be used to predict pollutant impacts at higher levels is a major, as yet unresolved question, the most frequently used method in ecological risk estimation is the quotient method (Falco & Moraski 1989b). This method compares a toxicologic benchmark such as the acute LC50 value to a calculated or measured exposure concentration to provide an estimate of risk. The reason for the frequent use of the quotient method is that for most chemicals the LC50 value is the only toxicity data available (this applies especially to fish). When there is no other data but the LC50 for the organisms of one community level, it is not possible to construct a sophisticated multispecies dose - effect relationship function. O'Neill et al. (1983) have, on the basis of ecosystem models, argued that ecosystem responses are to a great extent determined by the most sensitive species of the system. These indications can be taken into account when deriving the reference value (LC50).

In spite of the many faults inherent in the quotient method, it has proved suitable when a quick assessment of a large number of chemicals is needed and the data available is scarce (Suter II 1986). Although all damages to the ecosystem are the object of this study, the substance's toxicity to fish was selected as an end point for the calculations. The reason for this choice was data scarcity.

When no other data but the LC50 is available, regulatory agencies have for the most applied a safety factor of 0.1 to the LC50 for a particular substance, to set a limit to its concentration in a given water body (Waldichuk 1985). When  $0.1 * LC50$  is adapted as the zero effect level and a log-linear relationship is assumed to prevail, a parameter describing the magnitude of an effect resulting from a particular quotient can be solved from the equation (Fig. 13):

$$EF_{AL} = 0.5 + 0.5 \lg(Q_{AL}) \quad (23)$$

$$\begin{aligned} & \text{when } 0.1 < Q_{AL} < 10 \\ & = 0, \text{ when } Q_{AL} < 0.1 \\ & = 1, \text{ when } Q_{AL} > 10, \end{aligned}$$

where

- $EF_{AL}$  = magnitude of effect on aquatic life,  
 $Q_{AL}$  = quotient  $C_{AL}/LC50$  in the water volume concerned,  
 $C_{AL}$  = benchmark concentration concerning aquatic life (mg/l)

There are fundamental differences in the models for calculating the resulting concentrations in rivers and lakes or treatment plants. In a river system, a continuous profile of maximum concentrations downward from the release point is calculated. Therefore, the magnitude of effect in a river system is solved through numerical approximation. Lake or treatment plant systems consist of subsequent basins, and only one concentration value is assigned to each basin. It can be argued that also releases resulting in a lake basin quotient of less than 0.1 may cause damages in the portion of a basin near the release point where the expanding plume may have a high pollutant concentration. This effect must be considered in outlining the basin system to be used in dispersion calculations.

The same damage function is used in determining the extent of a possible upset in a biological wastewater treatment system, but the EC50 value for activated sludge (or a corresponding value for other biological treatment systems), derived from practical experience or testing by the OECD method 209 (OECD 1987) or some modification of it (e.g. Volskay & Grady 1988,) is applied instead of the LC50. As for other treatment systems, the damage function must be defined according to the functional properties of a system concerned.

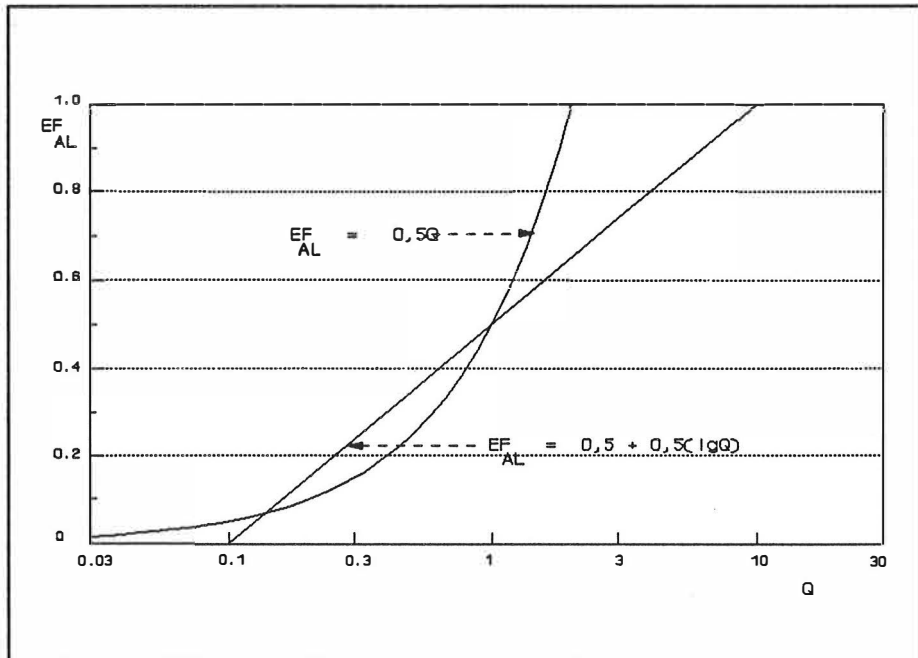


Fig. 13. The damage function used to relate the magnitude of effect ( $EF_{AL}$ ) and the calculated quotient ( $Q$ ) in surface water biological systems. A linear function is presented for comparison.

Because the  $LC50$  concentration varies with the time of exposure and different exposure times are used, a transformation to a fixed exposure time is needed before any quotients can be calculated. An equation constructed by French & French (1989) was adopted for this model. The equation is:

$$\lg(LC50_t) = b \cdot (\lg(t) - \lg(4)) + \lg(LC50_4) \quad (24)$$

where

$LC50_4$  = 96 hour (4 d)  $LC50$

$LC50_t$  =  $LC50$  at exposure time  $t$

$b = 0.8175$

$t$  = exposure time (d)

This equation was based on an analysis of a large database of toxicity data. When an exposure time is longer than four days, the four day  $LC50$  is used, because the lethal threshold concentration is usually reached within four days. The concentration resulting

from a release of material to a recipient does not remain stable for the four days, on the contrary, it changes constantly. Therefore, mistake of some degree is effected by the differences between the various recipients in temporal concentration profiles. It is possible to adjust the reference value to temporal concentration changes by using numerical integration, but in regard to the uncertainty of the parameters available, such an adjustment would appear unreasonable.

The LC50 values for a given chemical may vary by two or three orders of magnitude, depending on the species tested. The LC50 values can also vary considerably according to the life-cycle stage of the species tested and the sensitivity of that stage. The toxicity data is selected according to Landner's (1987) recommendations. Environmental variables, such as water temperature, hardness, pH, salinity, the dissolved oxygen concentration and the presence of metals have an effects on the toxicity of chemicals; however, there is not enough data for presenting the quantitative relationships between these variables. The effect of environmental variables must be taken explicitly into account when selecting the benchmark value. For example Mossman et al. (1988) concluded that in the case of the pesticide release to the river Rhine, the fish kill was most likely the result of chronic heavy metals exposure coupled with brief high concentrations of pesticide combinations. If several chemicals are included, a simple additive effect is assumed, if no other information is available.

Immiscible materials which are lighter than water (e.g. oil) form surface slicks on the water. Surface slicks threaten mainly birds and mammals in the water environment but may also cause pollution of shoreline and, when sinking or mixing with water, other aquatic life, too. For the sake of simplicity, the damage value of surface slicks is related to damages from water miscible hazardous substances. The damaged area for surface slick forming materials is calculated from the threshold value of injurious surface slick thickness. Oil is the most frequent surface slick forming pollutant, and the threshold value of 0.001 mm has been presented to oil (Rosen 1971). The calculation formula is:

$$A_s = M_s / (\rho \cdot d) \quad (25)$$

where

- $A_s$  = maximum area covered by surface slick (m<sup>2</sup>)
- $M_s$  = mass released to surface water (kg)
- $\rho$  = specific gravity (kg/m<sup>3</sup>)
- $d$  = threshold thickness for surface slick (m)

The magnitude of effects is assumed to be linearly related to the extent of the damaged area. In a lake system the magnitude of damages is calculated as a portion of a basin which can theoretically become covered by injurious surface slick resulting from the release concerned:

$$EF_s = A_s/A_B \quad (26)$$

where

$EF_s$  = magnitude of effects from surface slick in a surface water basin

$A_B$  = surface area of a basin ( $m^2$ )

If the effect for the first basin is more than 1, the surface area of the first basin is subtracted from  $A_s$  and the magnitude of effect is calculated for the second basin. This is continued until the last effect value is less than 1. In river systems the magnitude of effect is 1 for the length covered by surface slick.

There is an inherent margin of safety in drinking water standards (e.g. Cotruvo 1989). Therefore, it does not appear reasonable to apply the concentration-response equation in the assessment of risks to drinking water intake. Drinking water intake is likely to be halted if concentration of some chemical in the reservoir is close to the drinking water standard. The probability of a cessation of water intake and the resulting loss of benefits are the components of risk. If a release has occurred, the probability of a water intake cessation is assumed to be equivalent to the quotient of chemical concentration and the drinking water standard for that compound ( $C_{DW}$ ). Therefore, specific drinking water standards are linearly related to maximum concentrations calculated for a basin with drinking water intake. The damage function for drinking water intake is:

$$EF_{DW} = C_{s_{DW}}/C_{DW} \quad (27)$$

where

$EF_{DW}$  = magnitude of effects to drinking water intake

$C_{s_{DW}}$  = contaminant concentration in surface water at the point of water intake

In a river system, the calculated maximum concentration at the distance of water intake is used. This same damage function can be applied to other uses of water (e.g. industrial or agricultural) if the benchmark concentration is respectively changed.

### 3.3.3. Groundwater dispersed releases

Chemical concentrations in groundwater estimated by the method described in chapter 3.2.3 are compared to drinking water standards. It is assumed that the linear relation between a predicted concentration and drinking water standard reflects the extent of groundwater pollution when the particular scenario is realized. If there are several chemicals in groundwater, a simple additive effect is assumed, unless no other information is available.

Non-human biological damages are usually negligible when groundwater contamination is concerned. Only in case the groundwater is discharged into an extremely sensitive environment, the contaminated groundwater has the potential of causing ecological damages. No formal methods for evaluating ecological damages are presented concerning groundwater contamination, but heuristical evaluations are suggested in the User's Manual (Rossi 1991).

Releases of hazardous materials may lead to soil contamination even if no groundwater pollution is anticipated. This kind of a situation is probable when, due to soil properties, groundwater recharge is minute and contaminant sorption efficient. The effects of soil contamination are included by adding a separate term to groundwater damage value calculations.

### 3.3.4. Environmental persistence and bioconcentration potential

In addition to acute toxicity, the risk of detrimental effects due to a long term exposure to low concentrations of hazardous chemicals is recognized. When instantaneous releases are concerned, long term toxic effects are significant only if the chemicals persist in the environment. If a chemical is persistent and has potential to concentrate in the biological compartments of the environment, it is considered especially hazardous. The environmental effects of persistent chemicals are in this study considered in two separate phases: damages resulting from acute toxicity are evaluated according to the procedure described above and the factor related to the potential damages caused by chronic effects is added to this damage value.

Polychlorinated biphenyls (PCBs) and mercury are classical examples of bioconcentrating compounds. PCB compounds tend to accumulate in sediments in which they are subsequently transported to the water column due to the action of benthic organisms and water currents (resuspension). In spite of the low volatility, PCB compounds are liberated to the air and transported in substantial amounts over long dis-

tances.

Because the behaviour of a persistent chemical may be extremely complicated, dispersion and dilution assessments of instantaneous releases are not reasonable as for chronic hazards. When environmental concentrations are not calculated, valuations of the real damages cannot be made either. Indeed, the factor of chronic toxicity reflects more the anxiety about the increase of overall environmental contamination than the expected damages caused by the release concerned.

The environmental impairment potential of persistent and bioconcentrating compounds is calculated from release quantity, bioconcentration, persistence and chronic toxicity as follows:

$$V_{\text{CHR}} = M \cdot (\text{BCF})^2 \cdot (2 \cdot \text{PRS})^2 \cdot \text{TX}_{\text{CHR}} \cdot S_{\text{CHR}} \quad (28)$$

where

$V_{\text{CHR}}$	= valued long-term effects,
$M$	= release quantity (kg),
$\text{BCF}$	= bioconcentration factor (unitless 1-6),
$\text{PRS}$	= persistence factor (unitless 0-3),
$\text{TX}_{\text{CHR}}$	= chronic toxicity factor (unitless 0-5),
$S_{\text{CHR}}$	= scaling factor.

The scaling factor is used in adjusting the outcome of the calculation to the scale adapted to this model. The scaling factor is determined so that a 100 kg release of material with maximum values for all parameters is assigned a damage value of 1 000. Ensueing from this presumption, the scaling factor is roughly 1/650. This function comprises a valuation component which was not included in the damage functions for acute effects. This function is called a damage value function and its outcome constitutes by itself a part impact term. The chronic effects damage value is calculated to all releases regardless of the primary recipient.

The chronic effect component is designed to be a sensitive indicator and if the model gives implications of a high risk level, the result must be carefully studied using heuristical evaluations or more precise calculations. Unlike the revised HRS (Federal Register 1988), the model gives more weight to bioconcentration and persistence than chronic toxicity. This is due to the difference in the intended applications between the two models. While this model is centred on short term releases, the greatest emphasis in the HRS is on long term releases. Bioconcentration, persistence and chronic toxicity factors are determined by using the method implemented in the revised HRS.



### 3.3.5. Valuation of environmental damages

The damage functions described above are used for calculating the magnitude of damages to target populations, yet only the chronic effects component comprises an inherent valuation of damages. To render the discrete environmental damages comparable with each other, at least a relative valuation of all damages is needed. One possibility is to calculate the economic value of the damaged natural resources. For example Grigalunas et al. (1989a) have presented an economic loss evaluation model for calculating losses from chemical spillages in marine environments. The model accounts for the economic value of both consumptive (fishing, hunting) and nonconsumptive (e.g. viewing, photographing) biota losses as well as damages to public beaches. When incidental releases from wood processing industry are concerned, the losses of economic values are expected to be small; indeed, it is evident that the measurable economic losses are not a sufficient indicator of the extent of damages.

The concept of determining non-market values has been the subject of a great deal of research and not a few methods have been developed for the purpose (Sinden & Worrell 1979). Even when these methods are used, environmental hazards characteristically result in negligible monetary values, because many significant aspects are excluded (Schechter 1985). Shafer & Davies (1989), too, have argued that human judgment is indispensable in making decisions related to environmental problems. It seems obvious that a more relevant estimate of the value of a potential hazard can be achieved by using an undeterministic but consistent approach. O'Banion (1980) has presented a method of determining value functions to environmental impacts. As for the present study, a strict formal compliance to that technique was not considered reasonable, since a group opinion is apparently needed in this kind of problems.

The Delphi technique (Dalkey & Helmer 1963) offers a simple and flexible method for assessing the perceived value of potential hazards. The general procedure in the Delphi technique is to ask each person in a group for data and then, through successive rounds of feedback, to encourage them to revise their data toward a common consensus value. Direct face-to-face confrontations are deliberately avoided through the use of mail questionnaires. In this context a group of experts representing different societal groups is given descriptions of various hazard scenarios, and each person is asked to value these described hazards. After reaching a consensus among group members, damage value functions presenting the value of damage as a function of damage extent can be defined. The impact term of the index is a sum of values resulting from a release concerned.

There are considerable differences in risk perception between experts and the public. Slovic (1987) has emphasized the concept that small accidents may act for the public as

signals of further and possibly catastrophic mishaps; that is why the perception of certain domains of accidents is insensitive to scientific data.

One way of ensuring a better consistency between experts' and the public's perception is to consider also the higher order impacts in valuing the predicted damages. For example, the accident at the Three Mile Island nuclear reactor in 1979 did not cause a single death, and few if any latent cancer fatalities are expected. Despite that, the accident accumulated enormous costs to the nuclear industry and society through stricter regulations, a reduced operation of reactors worldwide, greater public opposition to nuclear power and reliance on more expensive energy sources.

It would appear reasonable for enterprises to recognize the fact that, the risks of environmental pollution involved in the management of hazardous materials are regarded as high by the public and the social costs of accidents may grow extremely high in the long view. Therefore, all methods of assessing environmental risks in industry should be relatively insensitive to magnitudes but sensitive to certain damage qualities. In this index system, the higher order impacts are incorporated through a simple procedure: a set of them is listed in the questionnaires mailed to the group of experts conducting the valuation. These higher order impacts consist of research and information costs, possible sanctions or claims and image losses.

In addition to the higher order impacts, the following subjects are considered in cases of releases to the air, when reference distances are determined:

- number of people as a function of distance and point of compass,
- variability of wind direction, and
- vulnerability of the population.

The employees at a facility are usually the first to be exposed to toxic releases. The risk to them is regarded as part of work safety evaluations and it is therefore not typically considered in environmental risk analyses. When health effects are concerned, the potential of off-site effects should result in the predefined value of 1 000. Therefore, the distance to the nearest residence or public building is a typical reference distance.

As for nuisance effects, the number of potentially exposed people is weighted according to the frequency distribution of the wind direction. The two predetermined zones are divided into 90° sectors and the human population in each sector and zone is determined and weighted, using statistics for the wind direction in the study area. After that, the damage value of an exposure to the nuisance effects of bad smell or dirtying particles is assessed for two distances.

Concerning releases to surface waters or groundwater, the magnitude of effects describing the portion expected to be damaged is calculated using a specific damage function. The purpose of the valuation procedure is to adhere scores describing the

assumed value loss in the case of a release scenario with the magnitude of effect 1 for a resource concerned. For a river system, three subsequent sections are valued separately.

Releases to surface waters may cause effects to wastewater treatment plants, river systems and lakes, estuaries or seas. Each of these effects is valued discretely and the total damage is summed from these values for each release scenario. Covering all releases to surface waters, the following damages are considered:

- upset of wastewater treatment system,
- fish kill,
- mortality to egg and larval stages of fish,
- damages to other aquatic life,
- shutting down of municipal or industrial water intake,
- prevention of recreational use, and
- clean-up, research etc. costs.

Groundwater resources are valued for the threatened part of aquifer. The factors to be considered in the valuation are:

- potential user population,
- substitute groundwater resources,
- existent groundwater discharge structures,
- contaminant removal possibilities,
- groundwater quality control measures,
- clean-up, research etc. costs, and
- self purification capacity.

Guidelines for the evaluations are given in the User's Manual (Rossi 1991). The parameter accounting for the value of long-term risks related to the persistent and bioconcentrating characteristics of released chemicals is defined according to chapter 3.4. and added to the impact term of each release scenario.

Health damages are not assumed to be caused in any other instances than in toxic releases to the air. As for releases to surface or groundwater, the consumption and other use of water is presumed to be prohibited by authorities. Although health risks pertaining to water recreation are not likely when short term releases are concerned, it can be assumed that recreational use would be prohibited if the chemical concentrations were close to drinking water standards. For water recreation, the visual amenity of water is important (Heiberg & Hem 1989) and the impact on recreation needs to be evaluated even for non-toxic releases, when the effects on water colour are apparent. The colouring effect can be calculated by using the same procedure as for toxic effects, but the benchmark concentration and damage value must be adjusted accordingly.

### 3.4. Aggregation of submodels and formulation of output

The probability term presents the joint probability of all the scenarios of instantaneous releases defined in chapter 3.1. The impact term represents the expectation values of those release scenarios. Only continuous releases to groundwater and potential releases involved in fires or explosions are considered separately.

It is a common practice to describe a risk as a product of probability and consequences. When the probability can be considered in terms of the frequency of events per year, this is a means of providing an average yearly loss due to these events. Although theoretically questionable when rare events are concerned, it is a simple and readily understandable way of combining the probability and magnitude of hazards. When the total environmental risk adhered to a process unit is assumed to be the sum of the products of probabilities and the impacts of separate release scenarios, the index for a single process unit can be calculated from the following equation:

$$RI_i = \Sigma(P_{ij} \cdot Va_{ij}) + \Sigma(P_{ij} \cdot Vs_{ij}) + \Sigma(P_{ij} \cdot VIg_{ij}) + \Sigma VCg_{ij} + \Sigma(P_{ij} \cdot V_{CHRij}) \quad (29)$$

where

- $P_{ij}$  = probability term for release of material j from process unit i,
- $RI_i$  = risk index value for a single process unit i
- $Va_{ij}$  = value of airborne damages from release of material j from process unit i,
- $Vs_{ij}$  = value of surface water borne damages from release of material j from process unit i,
- $VIg_{ij}$  = value of damages from instantaneous release of material j to groundwater from process unit i,
- $VCg_{ij}$  = value of damages from continuous release of material j to groundwater from process unit i, and
- $V_{CHRij}$  = valued long-term effects due to the release of material j from process unit i.

A ranking of process units is based on risk indices. Because combining probability and impact terms through multiplication does not have a sound theoretical basis, a presentation of separate probability and impact terms is necessary, too. A two-dimensional graphic presentation typically used in risk analysis reports is built into the computer program.

## **4. Case study**

### **4.1. Description of test site**

The test site is located by lake Pien-Saimaa in southeastern Finland. The immediate part of the recipient consists of three basins (Fig. 14). Basin 1 is used for lumber storing and, in order to keep the basin water open, cooling waters are periodically discharged to it. Wastewaters from the production are discharged to basin 2 and both basins 2 and 3 are moderately polluted. The theoretical retention time in basin 2 is about 1.6 d and in basin 3 about 2.0 d. The water flow is maintained by pumping water from lake Suur-Saimaa to the western Pien-Saimaa. The water quality of surrounding areas of lake Saimaa is described by Kansanen et al. (1990).

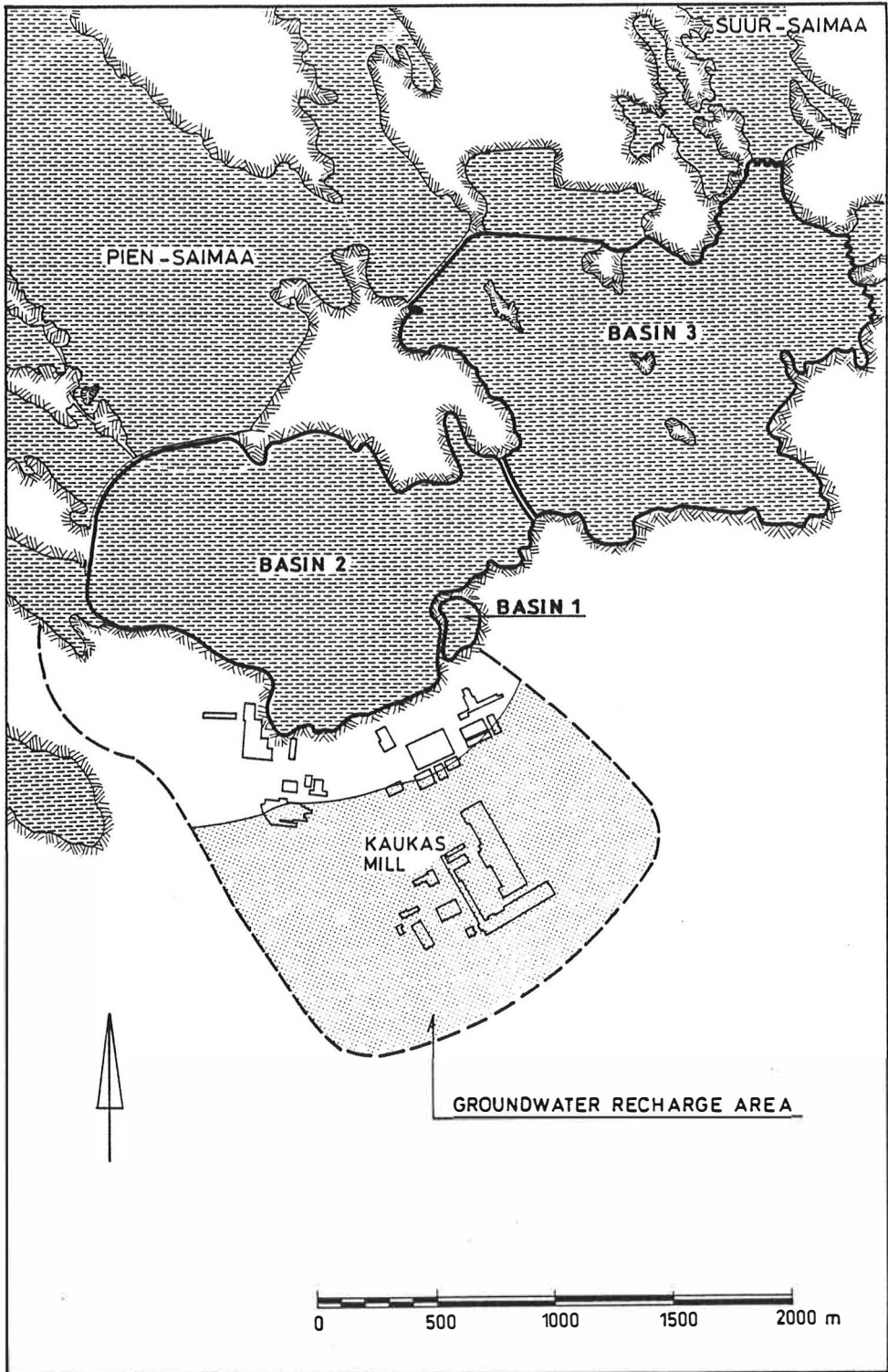


Fig. 14. Map of the study area.

The groundwater flow is confined by rock ridges; the total area inside groundwater divides is about 1.7 km<sup>2</sup>. The recharge area with sandy soils covers about 1.0 km<sup>2</sup>, while the rest of the area consists of artificial fill, pavements and buildings. The water discharge from this small aquifer is about 1 000 m<sup>3</sup>/d.

Chemical wood processing plants encompass a pulp production plant with a capacity of 335 000 t/a fully bleached pulp. The by-products comprise raw turpentine 400 t/a, natriumsulphate 5 500 t/a and soap. The soap is further processed in the chemical plant, which produces 8 000 t/a raw tall oil, 1 500 t/a neutral tall oil and about 200 t/a sitosterols. The paper mill's two production lines yield 335 000 t/a coated magazine paper. The power plants consist of two black liquor recovery boilers, two bark burning boilers, one supplement boiler and one gas turbine. In addition, exhaust gases from pulp production and condensate stripping are burned in a special boiler.

There is also mechanical wood processing industry in the same area. The plywood production plant and the sawmill were included in this study. Central storage, maintenance and transportation departments serve all plants, therefore they were considered as well.

Wastewaters are treated in an aerated lagoon but by 1992 an activated sludge or some corresponding treatment will be postulated by the authorities. The process wastewater discharge is about 5 000 m<sup>3</sup>/h. When treated in the aerated lagoon, the biological oxygen demand of the wastewaters to Saimaa is about 13 t/d (BOD<sub>7</sub>) and the total solids about 11 t/d. With the activated sludge facility in operation, the biological oxygen demand is assumed to be less than 4 t/d. The black liquor and bark burning boilers are equipped with electrical filters. Location of the plants is presented in Fig.15.

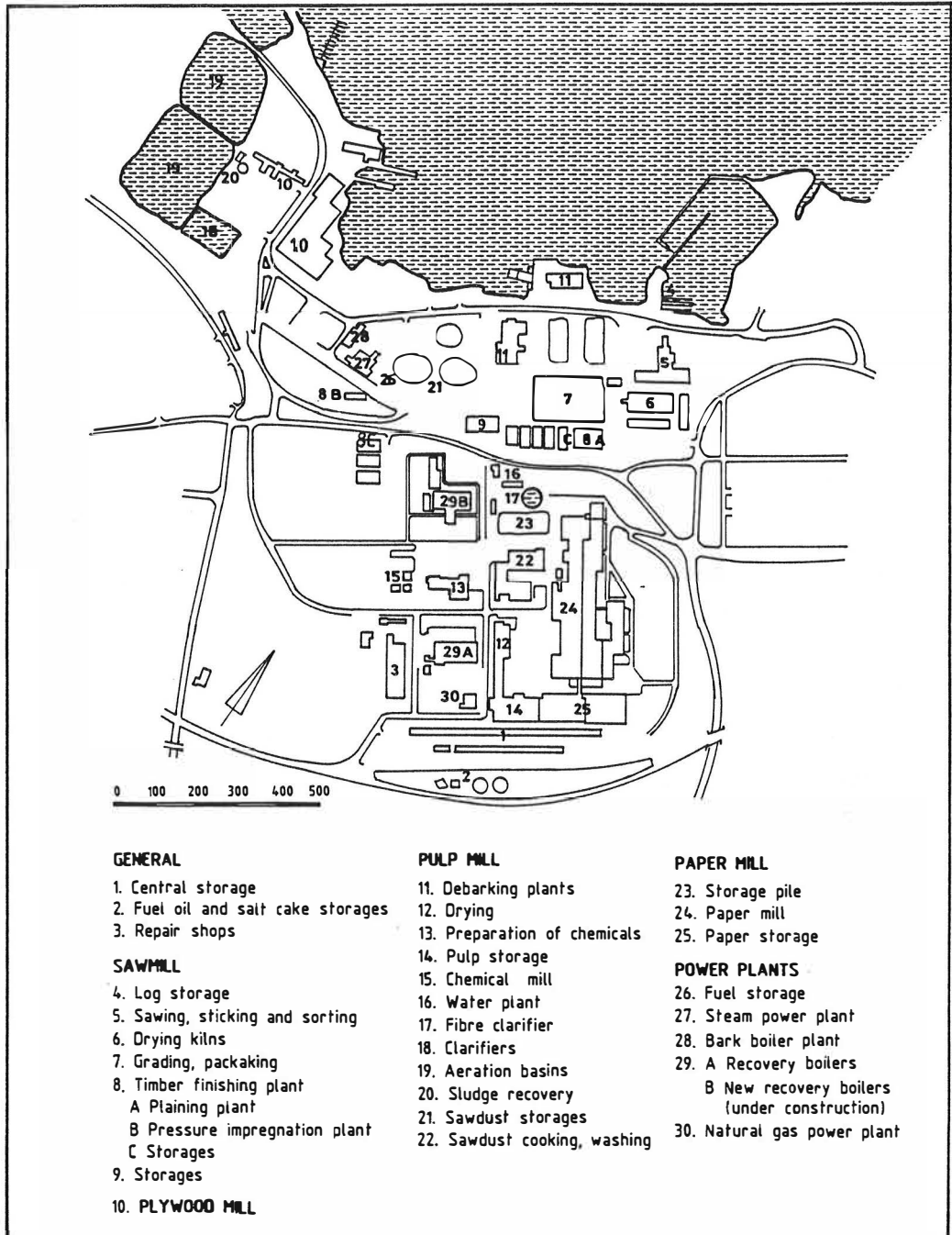


Fig. 15. Layout of the mill area



## 4.2. Description of data

An environmental risk screening procedure based on subjective assessments was carried out, in order to provide a rational basis for selecting the most important process units for the index calculations. The screening process consisted of 22 meetings lasting about two hours each. In addition to the author, 1-2 risk analysis experts from Industry Mutual and 1-4 persons from various organizational levels of Kaukas Ltd attended the meetings.

A total of 34 process units were analyzed. The main emphasis in selecting the units was on the quantity and quality of hazardous materials handled in them. In addition to the most important ones, a number of units with an apparently lower risk level were selected, in order to get more diverse data for the index tests. If there were several roughly units, only one was treated in the calculations. Liquefied gases ( $\text{Cl}_2$ ,  $\text{SO}_2$ ) excluded, because these systems have been studied as part of the company's safety management programme.

Data for release probabilities and quantity factors was collected in meetings with approximately the same number of representatives from various organizations as in the screening phase. The only difference was that the participants from Kaukas Ltd were from lower organizational levels and contributed a more detailed knowledge about the system analyzed. The data collection was supplemented with flow schemas and site inspections. In addition to the scored probability factors, the probability of the occurrence of a fire at the chemical plant and in its tank area were estimated. The probability of leakages from the sewage works and leachate from the dreg disposal pit was set to 1 because a leakage would probably be continuous. The expected leakage volume was estimated according to the guidelines of the User's Manual (Rossi 1991). The analyzed process units with unit specific data are presented in Appendix 1.

Environmental data on the chemicals in question was collected from literature when available. Little data on the environmental properties of process fluids was reported in the literature studied, and in many cases the toxicity values were inferred from properties of the main components. Experience about upsets of the present aerated lagoon due to exceptional releases was used for a retrospective calculation of critical concentrations for the materials concerned. Because there was no other information available, it was assumed that a critical concentration for activated sludge in the new wastewater treatment plant equals that of the present lagoon. For some fluids there were experimental data about their effects on the activated sludge pilot plant. When the toxicity of a material was apparently effected by a pH change, titration graphs were prepared with the water concerned. The critical pH values were set to 5.0 and 9.5 for both activated sludge and

aquatic life.

In principle, the benchmark values represent the LC50 (96h) values for fish when releases to a lake are concerned, the EC50 values to activated sludge as regards releases to a wastewater treatment plant, and drinking water standards in the case of releases to groundwater (Table 3). Because of the lack of data, many benchmark values had to be inferred from heterogeneous values reported in literature, or from values covering only a few components of a process fluid.

The benchmark values were linearly transformed to equal the concentration of the material in a particular process unit. The benchmark for total sulphur was used in calculating the groundwater effects of dreg disposal pit leachates and of wastewater leakages from wastewater works. The effects of particles from the recovery boiler and of odorous gases releases from the cooking department were estimated as functions of distance. This was made on the basis of previous experience, no dispersion calculations were carried out.

Table 3. The benchmark values of the chemicals and process fluids used in the index calculations.

Material	Benchmark values mg/l	Target <sup>2</sup>	Basic data source <sup>1</sup>
Acetone	1 500	L	Nikunen et al. (1986), Verschuieren (1983), LC50(24h) trout 6 100 mg/l
Erco-fluid	1 000	AS	Kaukas Ltd, pilot experiment
Phenolic resins with biocide	350	AS	Michelason (1982), 2,3,4,6-tetra-chlophenol inhibition of anaerobic bacteria 25-50 mg/l
Glyoxal (40 %)	100	AS	Hommel (1987), bacteria 100-1 000 mg/l
Hexane	1 000	L	Hommel (1987), water organisms over 1 000 mg/l
Methanol	4 500	L	Nikunen et al. (1986), LC50(48h) trout 8 000 mg/l
Black liquor <sup>3</sup>	50	L	titration
Black liquor	200	AS	experience
White liquor	200	AS	experience
Green liquor	200	AS	experience
Sulphuric acid (98 %)	60	AS	titration
Sulphuric acid (98 %)	10	L	titration, Hommel (1987), LC fish
Sodium hydroxide (50 %)	50	L	titration, Hommel (1987), LC fish
Sodium hydroxide (50 %)	50	AS	titration
Evap. condensates	50 000	AS	Kaukas Ltd, pilot experiment
Soaps	5 000	AS	Kaukas Ltd, pilot experiment
Soaps	1	L	Nikunen et al. (1986), fatty and resin acids, LC50(96h) fish 1 mg/l
Raw turpentine	23	L	Nikunen et al. (1986), alfa-pinene, LC50(48h) Daphnia magna 41 mg/l
Raw turpentine	100	AS	Sierra-Alvarez et al. (1990), alfa-pinene, inhibition of anaerobic bacteria 75 mg/l
Tall oil	0.01	GW	1 % of LC50(96h)-value of fatty and resin acids
Tall oil	100	AS	Sierra-Alvarez et al. (1990), abietic acid, inhibition of anaerobic bacteria 75 mg/l
Mineral oils	25	AS	Tabakin et al. (1978), 25 mg/l
Mineral oils	0.05	GW	National Board of Health (1980)
Sinesto B	40	L	
- trimethylcoco- ammoniumchlorid (14 %)			Kymin paperiteollisuus Ltd, LC50(96h) Salmo gairdneri 6 mg/l
-sodium-2-ethylhexanate (26 %)			Kymin paperiteollisuus Ltd, LC50(96h) Salmo gairdneri 99 mg/l
Total S	0.1	GW	VROM (1983)
Mineral oils (surface slick)	0.001 mm	L	Rosen (1971)

- \*) L=lake, AS=activated sludge, GW=groundwater, A=air  
\*\*) Data in the reference collected from several sources  
\*\*\*) Weak black liquor
- 

Only rough estimates of the values of reaction coefficients were available. An overall removal rate of 0.01/d was assigned to all organics in wastewater and lake systems. In groundwater a system, the removal rates of 0.01/d in the upper zone and 0.001/d in the lower zone were given to tall and mineral oils, whereas no removal was taken into account as regards other releases to groundwater. Since there was no data available on the sorption characteristics of tall oil, a retardation factor of 1 was adopted. The maximum soluble concentration of fuel hydrocarbons in groundwater was set to 10 mg/l, relying on practical experience reported by Frankenberger et al.(1989). The solubility limit was needed in the assessment of the groundwater effects of instantaneous spills.

For the long-term effects component, hexane was attached a biomagnification factor of 4 and a persistence factor of 1. The biocide in plywood glue contains tetrachlorophenol, which was assigned a biomagnification factor of 4 and a persistence factor of 3. The biomagnification factors were obtained from Wang et al. (1987) and persistence factors from a report by MITRE corporation (MITRE 1986).

Data of the future wastewater treatment plant was used in the calculations (Table 4). The effective volume of the primary clarification basins and the equalization basin was assumed to be 80 % and in the aeration basin 100 % of the total volume. In the case of releases to the lake, mixing was always supposed to be 100 % in basin 1. In basins 2 and 3 the releases were assumed to mix only with upper (0-3 m) or lower (>6 m) layers, depending on the specific gravity of the material released. The purpose of the above practice was to reflect stagnation situations, when ice or the temperature gradient prevent efficient mixing. The volumes of the water layers were calculated from depth contours. Surface areas of the lake basins were estimated from a map with the scale 1:20 000. Population data was collected from Lappeenranta city planning office and wind statistics from Lappeenranta airport.

Table 4. Environmental parameter values used in the index calculations.

Parameter	Value	Application
<b><u>Wind direction weight</u></b>		
- sector 0-90	1.2	Airborne releases
- sector 90-180	0.9	"
- sector 180-270	0.9	"
- sector 270-360	1.0	"
<b><u>Wastewater treatment plant</u></b>		
- primary clarification vol.	14 400 m <sup>3</sup>	Releases to wastewater plant
- equalization basin	53 000 m <sup>3</sup>	"
- aeration basin	120 000 m <sup>3</sup>	"
<b><u>Lake recipient</u></b>		
- basin 1 volume	150 000 m <sup>3</sup>	All but surface slick
- basin 1 surface area	30 000 m <sup>2</sup>	Surface slicks
- basin 2 volume	3 600 000 m <sup>3</sup>	Light materials
- basin 2 volume	700 000 m <sup>3</sup>	Heavy materials
- basin 2 surface area	2 000 000 m <sup>2</sup>	Surface slick
- basin 3 volume	3 900 000 m <sup>3</sup>	Light materials
- basin 3 volume	130 000 m <sup>3</sup>	Heavy materials
- basin 3 surface area	2 200 000 m <sup>2</sup>	Surface slick
<b><u>Groundwater system</u></b>		
- groundwater discharge	1 000 m <sup>3</sup> /d	All gw. dilution
- rainwater infiltration	0.001 m/d	"
- depth of upper vadose zone	0.5 m	Long term releases
- depth of lower vadose zone	8.0 m	"
- soil porosity	45 %	"
- groundwater flow	0.14 m/d	Short term releases

Data for the environmental values was generated by applying the principles of the Delphi method (Dalkey & Helmer 1963). Nine separate damage scenarios were specified and described by the author of this study. The descriptions were mailed to a group of 9 experts representing environmental authorities, industry, insurance and consultants, who then valued the described damages assigning the scores from 0 to 100. After that, these scores were multiplied by 10 to equalize the scale with the index. Out of the long-term effects of persistent compounds, only the scaling factor was evaluated by the team, for the damages in question are otherwise inherently valued in the model. Six categories of damages were described for the release scenarios:

- fish kill,
- groundwater contamination,
- disturbance of wastewater treatment plant,
- image losses,
- nuisance, and
- economic losses.

In the first phase the experts assigned scores to each damage category described. They also had the opportunity of presenting their own arguments. Then a meeting was arranged, where the results of the first round were presented anonymously, and the experts discussed the problems and arguments of the task. Next, a new inquiry was made, after which the team gathered again. On that occasion it was agreed that the median values of the second set of results were the proper consensus values to be used in the index calculations. In addition to these total effect values, an extra round for estimating the economic effects pertaining to the accident scenarios was carried out among seven experts of the group. The consensus values for the economic effects were scaled so that the sum of the scores equalized that of the total effects scores.

Supposing a simple additivity of the various components of valued damages, a total value score was calculated for wastewater treatment plant disturbances, each lake basin and the aquifer beneath the site. For air dispersed nuisances, two scenarios with different numbers of exposed people were valued (Table 5). The damage scenario "Disturbances on wastewater treatment plants causing slight licence violation" was not applied in the index calculations.

Table 5. Damage valuation results.

Damage description	Valuation of total effects			Valuation of economic effects		
	$\bar{x}$	s	Consensus value	$\bar{x}$	s	Consensus value
Toxic effect in lake basin 1	26.9	15.1	21	5.0	5.2	4
Toxic effect in basins 1 and 2	75.9	27.1	65	30.0	20.6	42
Toxic effect in basins 1 - 3	116.7	42.4	110	45.8	26.8	47
Disturbance of wastewater plant causing slight licence violation	81.7	33.0	70	40.4	31.4	26
Upset causing a two week disorder of wastewater plant	139.4	45.7	150	350.2	174.0	360
Release of odorous gases exposing 1000 people for 1 week	119.2	45.7	100	24.8	25.4	28
Release of odorous gases exposing 10000 people for 1 week	158.9	64.6	140	74.1	66.6	80
Release of nuisance particles exposing 1000 people	153.3	65.7	130	130.7	116.6	136
Contamination of the aquifer	169.4	88.7	150	234.9	109.0	215

The specific damage distances were derived from nuisance effect values using meteorological and residential statistics on the area. The effective distances, derived from previous experience, were compared to these reference distances, and the effects on aquatic life in lake basins were summed (Fig. 16). The distance from the potential release point to the closest site boundary was taken as the reference distance for airborne toxic releases, but because chlorine and sulphur dioxide were excluded, no process units comprised gaseous or volatile toxics that would impose hazards to off-site people. The impact term for the wastewater treatment plant and groundwater effects, is simply the product of an adherent value and an outcome of the damage function.

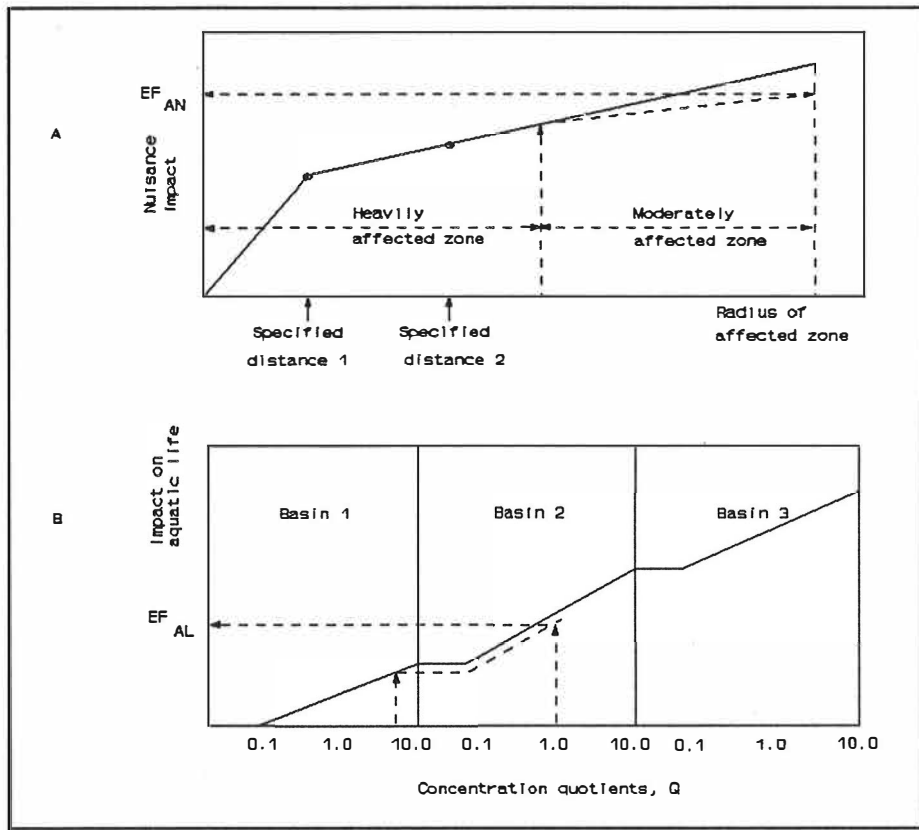


Fig. 16. Illustration of damage value assessment. A) Releases of odorous gases into the air B) Releases to surface waters. The dotted lines stand for example scenarios.  $EF_{AN}$  = magnitude of nuisance effect from airborne release.  $EF_{AL}$  = magnitude of effect to aquatic life.  $Q$  = relation of calculated concentration to benchmark concentration.

In addition to short-term damages, potential long-term effects were evaluated using the method prescribed in chapter 3.3.5.

#### 4.3. Results

The probability terms that were created by using the scoring method ranged from 0.25 to 0.04 (Fig. 17). They proved highest for the odour control system, the tall oil storage tank, the turpentine system and the sulphuric acid storage tank at the chemical department of the pulp mill. The unsaponifiable fraction extract system on the chemical plant and the



pulp digester received the smallest probability terms. When all probability terms are taken into account, the range is 0.001 - 1. Here the smallest figures are for the probability of fire at the flammable liquid tank farm and the chemical plant. The probability of 1 was assigned to the production of leachate from the dreg disposal pit and to leakages from the wastewater works.

Measured by the impact terms, the process units take a different order. The release of odorous gases drew the highest impact term, followed by the black liquor tank. Also an event of minor probability - fire at the chemical plant's tank storage area, - received a high impact term value.

Other process units of potentially high impacts were the tall oil storage tank, the wastewater works, the sodium hydroxide system, and the white liquor tank. The high value of the impact term for the chemical plant was due to the long-term effects component.

On the other hand, the impacts of short-term releases from the wood preservation system at the sawmill and from the fuel tanks nearby, but not on the lake, appeared limited. This can be explained by the fact that in these areas there is no significant groundwater recharge. Therefore, a chemical discharge onto the ground would cause only small clean-up costs.

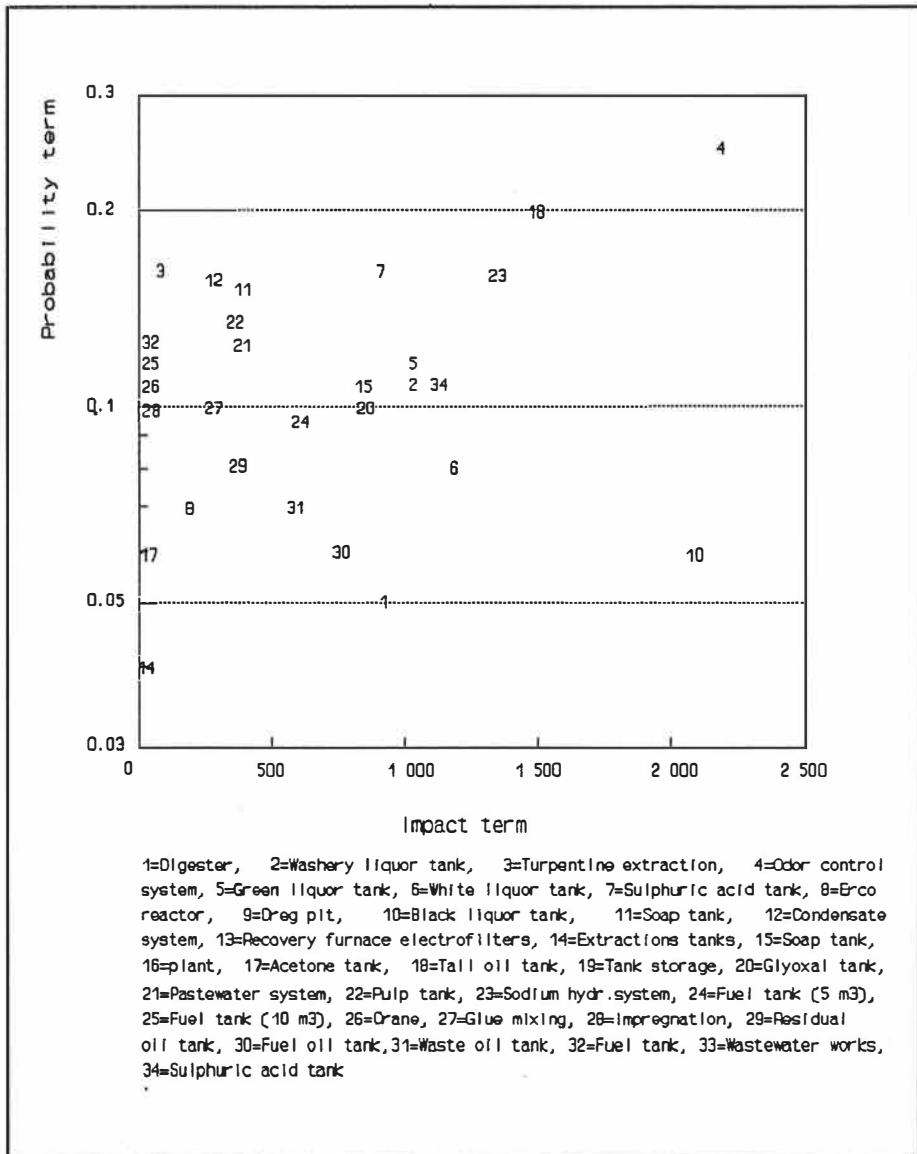


Fig.17. The scored probability terms with the respective impact terms. The numbers refer to the process units listed in Appendix 1.

Due to the influence of the probability term of 1, the wastewater works (33) and the dreg disposal pit (9) can be reported to have the highest environmental risk index values (Fig. 18). The other high risk process units are the odour control system (4), the tall oil storage tank (18), the sodium hydroxide system (23) and the sulphuric acid storage tank (7).

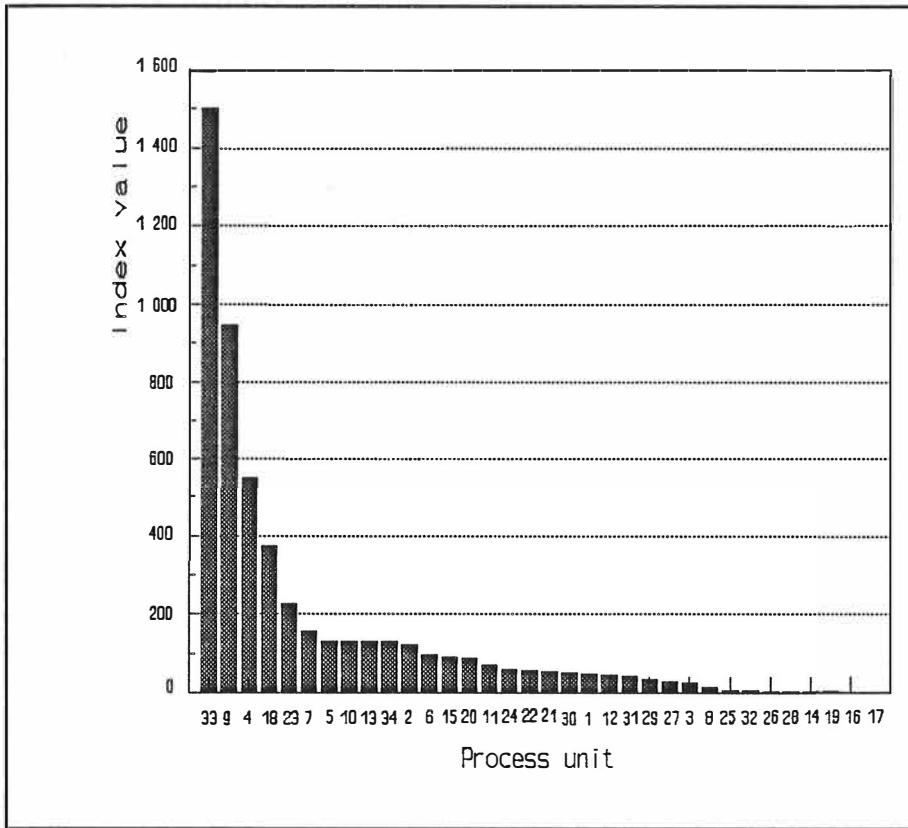


Fig. 18. The environmental risk indices of the analyzed process units. The numbers of process units correspond to those listed in Fig. 17 and Appendix 1.

The economic implications of accidents appear as especially important from the viewpoint of industrial enterprises or insurance companies. Wastewater treatment plant disturbances were estimated to have the potential for great economic losses, and these release scenarios appeared prominent (Fig. 19). On the other hand, process units with the potential for releases causing nuisance to people were rated lower.

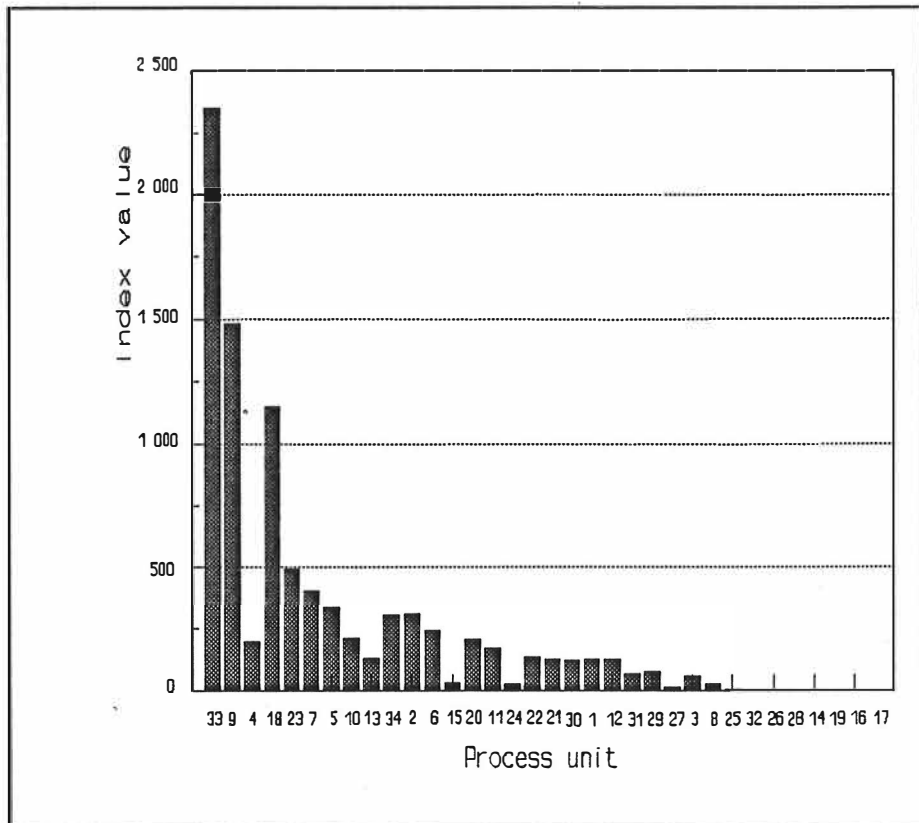


Fig. 19. The environmental risk indices of the analyzed process units with the impact term calculated from economic consequence estimates. The numbers of the process units correspond to those listed in Fig. 17 and Appendix 1.

## 5. Evaluation of index performance

### 5.1. Sensitivity tests

Sensitivity analyses involve systematical changing the values of one factor or a specific combination of factors to see how other variables are affected. The analysis can be used for testing the robustness of a model to unrelated, essentially random changes in the values of the critical variables. The procedure can also be applied to examining if the variables have been sufficiently weighted. Random changes may be the result of measurement errors or changes in other apparently unrelated variables. However, if a variable is so lightly weighted that it has no significant effect on the model's result, it might as well be excluded. This difference between a model's abstract structure and its structure in practice may be crucial for its effectiveness. Therefore, it is important to carry out sensitivity tests with data according with actual values.

Sensitivity tests of complex models can be performed stepwise: the sensitivity of submodels is tested first and the effect on the final outcome of changes in submodel results is examined after that. When the final outcomes are studied, the results of the sensitivity analyses of complex models do not appear unambiguous. In the absence of systematic testing, multiple variables may confuse the results, and the size and complexity of these models makes a visual comparison of one set of outputs with another difficult. Hence, for isolating the effects of specific variables, systematic comparison and numerical sensitivity indicators that summarize the measuring of various arrays of data against each other, are needed.

Alexander (1989) has presented several sensitivity indicators which can be used in testing complex decision models, whose outcomes are aggregations of multiple variables. Two of these indicators are designed to provide a reading of the difference that varying a selected factor will make in the outcomes expressed in a rank ordering of priorities. Alexander's  $A$  resembles Spearman's  $r$ , but is standardized between 0 and 1. Thus, 0

represents no change, while 1 indicates a complete reversal in ranks, that is, the maximum possible sensitivity. The random value of Alexander's A is 0.5. Alexander's A calculation formula is:

$$A_{Al} = \frac{\sum(x_{ik} - x_{ij})^2}{\sum_{\max}(x_{ik} - x_{ij})^2} \quad (30)$$

where:

$A_{Al}$	= Alexander's A sensitivity indicator
$x_{ij}$	= rank of alternative i with variable at (previous) value j
$x_{ik}$	= rank of alternative i with variable at (changed) value k
N	= number of alternatives (process units)

Beimborn's B shows the average change in the ranking of the alternatives when the selected variable is changed. The formula is:

$$B_{Be} = \frac{\sum(x_{ik} - x_{ij})^2}{N} \quad (31)$$

where the parameters are the same as in Alexander's A.

This indicator is not standardized and its values and distribution will change with the number of alternatives. According to Alexander (1989), this is quite a sensitive indicator.

The sensitivity tests of this index system are carried out in separate phases. First, the probability term's sensitivity to changes in individual factors is evaluated on the basis of the scores given in practice. Secondly, the sensitivity of process units' ranking to changes in the probability term, the dispersion and toxicity parameters as well as valuations of the damages is tested by assigning various weights to these parameters and employing the indicators described above. The effect of the release quantity is not tested because of its heterogeneity. This effect is, due to the dilution models applied, related to the effect of the reference concentration. A total effect valuation of the damages is applied in all sensitivity tests.

Comprehensive descriptions of the sensitivity tests of dispersion models are not presented here, because the tests appear as trivial due to the simple structure of the models. The following conclusions could be drawn on the basis of the sensitivity tests of the dispersion models:

- the release time has a minor effect on the concentration distributions in a wastewater treatment plant and lake basin system. That is because the differences in release times are small when compared to the retention times

- in the two systems,
- the overall removal rate (degradation+volatilization etc.) has a relatively small effect on concentration distributions in wastewater plant and lake systems due to the short time frame required for diluting the releases to no-effect concentrations, and
- retardation and degradation appear significant when long term releases of organics to groundwater are considered.

Factors related to material transfer, transportable containers and joints and gaskets were the most effective discriminators between the various process units as measured by probability term values (Table 6). The factors pertaining to reactions or sequential processes were given only in a few cases but when given, they had a high weight on the probability term. Judging by this research, the factors of batch reactions or extreme temperatures seem unnecessary, for no scores were assigned to them.

Table 6. The ranges, averages and standard deviations of the penalty factors of the probability term in practical application.

Factor name	Range	Average	Standard deviation
<b>General factors</b>			
material storage and physical processing	0.00 - 0.50	0.36	0.13
single continuous reactions or extract phases	0.00 - 1.30	0.12	0.33
single batch reactions or extract phases	0.00 - 0.00	0.00	0.00
multiplicity of reactions with same equipment or subsequent processes	0.00 - 0.80	0.08	0.21
material transfer	0.00 - 0.75	0.43	0.33
transportable containers	0.00 - 0.50	0.17	0.24
washings and emptyings	0.00 - 0.30	0.04	0.09
<b>Special factors</b>			
low temperature	0.00 - 0.00	0.00	0.00
high temperature	0.00 - 0.00	0.00	0.00
temperature fluctuations	0.00 - 0.30	0.05	0.12
corrosion and erosion	0.00 - 0.30	0.04	0.08
joints and gaskets	0.00 - 0.60	0.14	0.18
fatigue, vibration, foundations and support systems	0.00 - 0.40	0.06	0.12
processes or reactions difficult to control	0.00 - 1.50	0.11	0.34

The credit factors (Table 7) had quite a uniform effect on the discriminative character of the probability term. Recovery tanks and basins had a crucial importance in diminishing the potential of a discharge out of some systems, e.g. the Erco chlorine dioxide reactor and extraction vessels. On the whole, the personnel related factors received small values (high effect) but there was only little difference between the various process units, and the discriminating effect was small. The personnel related credit factors reflect more the site specific operation practices than the operation of single process units. Emergency power was the only credit factor with no effect on the probability term.



Table 7. The ranges, averages and standard deviations of the credit factors of the probability term in practical application.

Credit factor	Range	Average	Standard deviation
Pressure vessels	0.90 - 1.00	0.99	0.04
Non-pressure vessels	0.90 - 1.00	0.97	0.05
Transfer pipelines	0.80 - 1.00	0.97	0.06
Safety basins, walls etc.	0.70 - 1.00	0.98	0.07
Spill alarm and prevention systems	0.85 - 1.00	0.96	0.05
Recovery tanks or basins	0.45 - 1.00	0.90	0.16
Process alarm systems	0.90 - 1.00	0.98	0.03
Emergency power	1.00 - 1.00	1.00	0.00
Release risk assessments	0.90 - 1.00	0.99	0.02
Emergency shut down	0.95 - 1.00	0.99	0.03
Computer control	0.85 - 1.00	0.99	0.03
Operation instructions	0.90 - 1.00	0.97	0.04
Control	0.95 - 1.00	0.99	0.02
Management attitude	0.90 - 1.00	0.93	0.04
Environmental protection organization	0.90 - 1.00	0.91	0.03
Training in pollution control	0.90 - 1.00	0.92	0.03
Environmental protection in maintenance operations	0.95 - 1.00	0.97	0.02

Exponential weights were assigned to four model parameters to test the sensitivity of the model outcome to changes in these parameters (Table 8). The magnitude of the weights was determined so that approximately +100 % and -50% changes resulted in extreme values of a parameter.

Table 8. The original ranges, tested weights and resultant ranges of the parameters applied in the sensitivity tests of the model.

Parameter	Original range	Weight	Modified range
Probability term	0.001-1.00	1.10	0.0005-1.00
	0.001-1.00	0.90	0.002-1.00
Reference concentration	0.02-50 000	1.07	0.02-100 000
	0.02-50 000	0.94	0.03-26 000
Effective diluting volume	$(1-3\ 900)*10^3$	1.05	$(1.4-8\ 300)*10^3$
	$(1-3\ 900)*10^3$	0.95	$(0.7-1\ 800)*10^3$
Damage value	40-1 500	1.10	58-3 117
	40-1 500	0.90	28-722

The index outcome appeared quite robust to changes in the weighting of the tested parameters (Table 9). Although the overall sensitivity was low, it is evident that changes in the reference concentration or diluting volume have a greater effect on the final rankings than changes in the probability term or damage values. This is not surprising, since probability and damage values varied only slightly in the main body of data. Most of the probability estimates were generated by using the scoring system, and they did not vary much. In the light of this analysis, the sensitivity of the probability term could be greater. The small effect of damage values is understandable, because most of the damages were directed to the wastewater treatment plant or groundwater which were assigned the same damage values.

Table 9. Summary of the sensitivity analysis of the model outcome.

Parameters	Weight	Alexander's	Beimborn's
		A	B
Probability term	1.10	0.002	0.71
	0.90	0.001	0.41
Reference concentration	1.07	0.008	3.15
	0.94	0.018	6.94
Effective diluting volume	1.05	0.015	5.59
	0.95	0.005	2.06
Damage value	1.10	0.002	0.71
	0.90	0.007	2.65

The weak point in environmental analyses is typically the synthesis of the discrete impacts on air quality, human health, non-human biology etc., converting them into some measure of the relative desirability of alternatives. These problems emerged also in the present study during the procedure of determining the damage value. A possible way of avoiding the risks of comparing what would seem incomparable is to use methods based on set theories and system analyses.

For ranking various chemicals, Halfon & Reggiani (1986) have presented a procedure consisting of a set of measurements. These measurements are considered as elements of a vector, and the ranking is obtained by partially ordering the vectors representing each chemical. Halfon (1989) has tested this method also for ranking hazardous waste sites. It recognizes that not all items can be compared with each other in terms of environmental hazards when several criteria are used. In fact, the higher the number of criteria, the higher the probability that contradictions in ranking exist between the criteria. Halfon et al. (1989) have developed a computer algorithm for displaying results of ranking exercises in the form of Hasse diagrams.

For the vectorial approach, the scalar indices of the process units were decomposed into four attributes:

- probability term,
- damages to non-human environment,
- nuisance effect, and
- economic losses.

The number of attributes was limited to four to keep the number of incomparable units reasonably low. Furthermore, it is easier to compare various environmental damages with each other than the economic values with environmental or nuisance effects.

The probability term was taken as a separate attribute because of the considerable uncertainty pertaining to its absolute numerical value. Although the absolute value of the probability term was considered uncertain, it was concluded that the term gives a good estimate of the process units' ordinal ranking. To prevent the extreme values from disguising the differences between the majority of process units, the probability term was divided into four uneven classes:  $< 0.01$ ,  $0.01 - 0.09$ ,  $0.10 - 0.49$ ,  $0.50 - 1.00$ . All the other attributes were equally weighted by dividing the raw data into four equal classes, which were assigned numerical values from 1 to 4 (Table 10).

Table 10. Data used in the vectorial ranking procedure. Number of process units as in Fig. 17 and Appendix 1.

Process unit N:o	Probability term	Non-human environment	Nuisance effect	Economic losses <sup>*)</sup>
1	2	2	1	3
2	3	2	1	3
3	3	1	1	1
4	3	1	4	4
5	3	2	1	3
6	2	2	1	3
7	3	2	1	3
8	2	1	1	1
9	4	2	1	3
10	2	3	1	4
11	3	1	1	1
12	3	1	1	1
13	3	1	3	3
14	2	1	1	1
15	3	1	1	3
16	1	2	1	2
17	2	1	1	1
18	3	2	1	4
19	1	4	1	4
20	3	2	1	2
21	2	1	1	1
22	3	1	1	1
23	3	2	1	3
24	2	1	1	2
25	3	1	1	1
26	3	1	1	1
27	3	1	1	1
28	3	1	1	1
29	2	1	1	1
30	2	2	1	2
31	2	1	1	2
32	3	1	1	1
33	4	2	1	3
34	3	2	1	3

\*) The economic value of lost material or production disturbances was excluded.

The Hasse diagram shows that the 34 process units have been ranked at six levels (Fig. 20). The six process units that involve the highest environmental risks in terms of the criteria of Table 8 are the odour control system, the dreg pit, the black liquor tank, the

tall oil storage tank, the chemical plant tank farm and the wastewater works. The units at the bottom of the diagram impose the least risk to the environment.

An overall comparison between the results from vectorial ranking and index values reveals no substantial differences in the ranking order. The Hasse diagram shows the uncertainties related in transforming the different sets of values to the same scale, because several parallel hierarchies were developed. The change in ranking order was most considerable for process units 19 and 21. Process unit 19 was characterized by a low probability of occurrence but extensive damage potential. The change in ranking reflects the uncertainty involved in calculating the index value by multiplying the probability and impact terms. As regards process unit 21, the change is mainly due to the roughness of data classification.

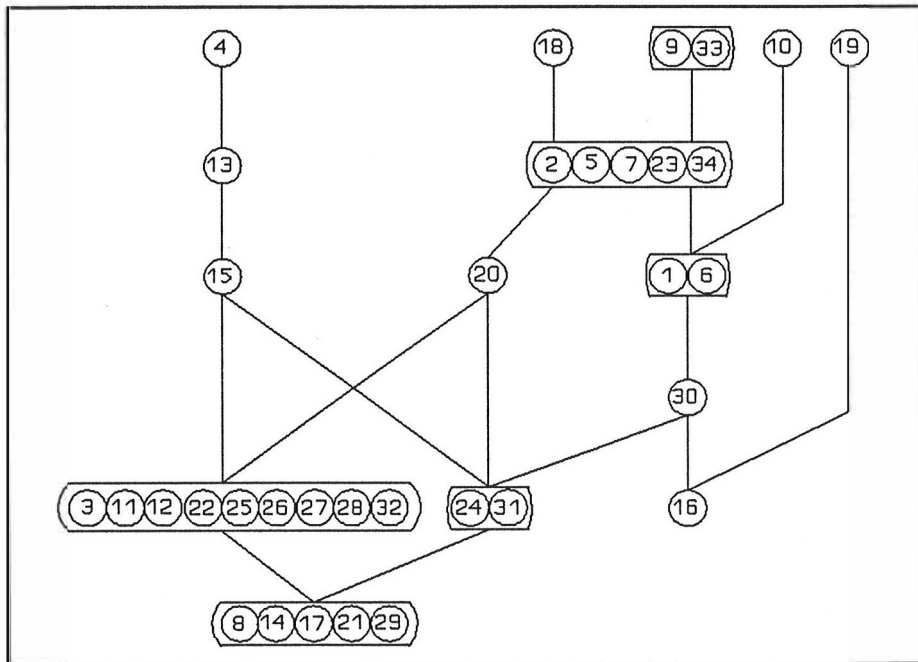


Fig. 20. The Hasse diagram of the process units ranked by using a vectorial method and data from Table 10.

## 5.2. Reliability of results

Attempts to validate the model performance can proceed along several lines. First, the concepts and theory embedded in the model should be appropriate for the problems addressed. Further, the specification of the equations, parameters and data used in the model should be the best estimates available. Because the construction of the model was based on an extensive review of literature and existing models, these general requirements should be fulfilled.

From another viewpoint, the model can be validated by comparing its estimates to corresponding situations in the real world. The most desirable way would be to compare the ranking of process units to a corresponding ranking of the same units based on previous reports on the environmental damages caused by each unit. This is obviously impossible because of the scarcity of data. Another possible method is to collect data from a larger population of corresponding process units. Here the data is more extensive than in the previous alternative, but its appropriateness appears questionable. This is evident for the reason that site specific circumstances have a decisive effect on the environmental risk level of a particular process unit. If this was not the case, there would be no sense in carrying out site specific environmental risk analyses.

Another problem is that if a certain type of process unit has been ascertained to impose substantial environmental losses, modifications are realized and the operating population of this process unit is different from the population which produced the main part of loss data. Also, the recorded spills have rarely been studied and reported comprehensively. Although it does not appear to be possible to use historical data to provide a definitive validation of this model, an attempt was made at comparing the data of this case study to the documented spill events in wood processing industry.

Data on accidental releases to surface or groundwaters was collected for the comparison from authorities responsible for the waters and the environment in Finland. The data covered 189 abnormal events, but in 33 cases the causative event was unidentified. In 83 cases exceptional pollution was due to a bypass of a wastewater treatment plant. Typical reasons for passing a treatment plant were mechanical or constructional failures or modifications of the system. Therefore, only 73 cases were considered relevant for this study. They were classified into 13 categories according to their causative events.

Another attempt at verifying the results consisted of a collection of data of critical near miss events involving the very process units assessed in this study. A total of 86 relevant critical events covering the years 1989-1990 were identified. Yet, because they did not

result in significant spills into the environment, no data concerning environmental damages can be achieved using this method. Consequently, only evaluations of the probability term are possible.

Since only direct causes of accidents are known, a proper classification corresponding to the factors in the probability term is not possible. In addition to the direct causes (e.g. operator errors), also origins of failures (e.g. poor instrumentation) and recovery failures (e.g. inadequate operation instructions) should be known. If all the contributing factors were known, each accident could be divided into several categories, which would make quantitative comparisons with the probability term possible. Because this was not true of this data, only qualitative evaluations of the model performance are presented together with statistics prepared from reported data and logbook notes (Table 11).



Table 11. Reported releases and critical events compared with average scores assigned to corresponding penalty factors in the index system.

Causative event	Number of events		Corresp. penalty factors	Average score
	reports	logbooks		
Overflow	14	23	Multiplicity of reactions with same equipment or subsequent processes	0.21
Leaking valve, pump, flange or gasket	12	23	Joints and gaskets	0.18
			+ material transfer	0.33
Leakage from incorrectly open valve or joint	10	3	Material transfer	0.33
Unloading a road tanker	9	3	Transportable containers	0.24
			+ material transfer	0.33
Washing or maintenance operation	8	5	Washings and emptyings	0.09
Leakage of a pipeline a hose	7	20	Material transfer	0.33
			+ transportable containers	0.24
			+ corrosion and erosion	0.08
			+ fatigue, vibrations etc.	0.12
Leakage from a tank	4	2	Material storage and physical processing	0.13
			+ corrosion and erosion	0.08
Towmotor transportation	1	0	Transportable containers	0.24
Frozing	1	1	Temperature fluctuations	0.12
Phase extraction	1	0	Single batch reactions or extract phases	0.00
Contaminated pulp	2	1	No proper penalty factor	
Electricity brake (Emergency power in credit factors)	1	4	No proper penalty factor	
Fire or explosion	3	1	Probability assessed explicitly	
<b>Total</b>	<b>73</b>	<b>86</b>		

There is a satisfactory overall consistency between the index results and the reported spill data. Also the critical events data agrees with the most with the reported spills data, but the relative proportion of events resulting from direct human failures is smaller in logbook data than among the reported spills. There are two possible explanations for the number of recorded critical, human failure related events in logbooks. First, such events are infrequent, but when they occur, they are likely to result in large releases. The second explanation is that incidents of this kind may not always be recorded in logbooks.

In spite of the overall consistency, the following shortcomings of the scoring system can be suspected on the basis the data:

- the potential of overflows caused by instrument failure or personnel oversight is not adequately discriminated,
- the potential of overflows caused by blockages due to material properties is not adequately discriminated,
- the release potential caused by removal of defective raw material is not discriminated,
- the score of washings or other emptying procedures is inadequately weighted.

In addition to wastewater and solids, the most frequently released materials were oils, sulphuric acid, resin glue, black liquor and sodium hydroxide. The spilled volume was reported only occasionally and no reliable calculations of average volumes or frequency distributions could be made.

Comparing predicted environmental damages to the impacts of real accidents is never a straightforward task; it always involves subjective elements, too. Grigalunas et al. (1989b) considered in their attempts at validating the National Resource Damage Assessment Model that the order of the magnitude of accuracy confirmed the model results. This same level of accuracy is generally recognized also in the impact component of safety analyses (van Kuijen 1990). In the data collected for the present study, environmental impacts of accidents were reported only in a few cases, and descriptions of the impacts were usually qualitative and superficial. Therefore, only rough conclusions can be drawn from the data. The importance of dilution conditions proved apparent from practical experience. Fish kill was reported even due to a release of 0.5 t of resin glue into a river system. On the other hand, however, an almost 100 t release of soap into the sea was reported to have caused colouring of water, but no fish kill.

## **6. Discussion**

### **6.1. Experiences of index use**

Environmental risk assessments have been commonly used for evaluating acute or chronic human health risks due to exposures to hazardous materials. On the other hand, the assessment of ecological risks or risks to natural resources is an emerging field of environmental management. Therefore, ecological risk assessment methods are as yet at an early stage of their development and lack official guidelines (Falco & Moraski 1989b, van Kuijen 1990). In estimates of the environmental risks involved in industrial operations, considerations of in-plant systems should also be included.

In this study, a new environmental risk index method was developed and tested. Applying the risk index method to assessments of the environmental risks in wood processing plants was encouraging. Most of the process units were easily evaluated by using the index. The time required for carrying out an evaluation of the probability and consequence terms varied from about half an hour to about three hours depending on the complexity of the system. Because each factor of the scoring system must be assessed separately, a significant amount of information which, in the case of a less formal method, would obviously have been skipped, was gathered. In addition to the scores of the probability term factors, a great deal of valuable information was gained during the discussions needed for the assignment of the scores.

Like all risk analysis methods, the probability term of this index is partly based on subjective expert judgements, which introduces a measure of uncertainty as regards the results. The extent of interanalyst error in the Dow and Mond indices outcomes was briefly studied by Andreasen & Rasmussen (1990). They found only small discrepancies,

which indicates that the reproducibility of both these indices is high. Although no tests were carried out concerning the interanalyst error in the present study, the error is likely to be small because this scoring system is less intricate than the Dow or Mond indices. Most of the score classes are unambiguously derived from technical details, and the selection of a score class is sensitive to subjective opinions only in few cases. The trade-off inside some score classes is quite large, that is why these scores may be liable to significant differences between analysts. Such factors include e.g. critical reactions or phase extractions.

Determining the release volume was problematic in many release scenarios. Process fluids are often viscous materials whose physical properties are affected by temperature. These materials are typically stored and processed as heated, but, after a release, a subsequent cooling often limits the migration of the discharged material. This phenomenon is especially complicated when a mixture of two different materials e.g. black liquor and soap is concerned.

Physical data for dispersion calculations was gatherable with reasonable resources. The most difficult task involved in surface waters dispersion is to determine the volume where the mixing of a pollutant is efficient. In this study, winter time conditions were presumed to prevail, and mixing only to the upper or lower water layer depending on the specific gravity of a pollutant was taken into account. The volumes of the recipient basins 2 and 3 were quite large, but when the results of damage valuations are considered, there was no need for more detailed calculations. The hydrogeological regimes were probably exceptionally well suited for the model, and the required data was supplied by a hydrogeologist without any special problems.

The most problematic part of the index calculation was the selection of reference concentrations for chemicals and process fluids. The environmental data on process fluids is scarce and the information available is often contradictory. The typical parameters which are routinely analyzed from process fluids are usually not the most significant ones in view of an environmental risk analysis. For example, the reduced sulphur compounds are obviously the most important pollutants in leaking sewage works, but typically only total sulphur is analyzed from wastewaters. The benchmark concentration of soap in the activated sludge pilot plant was surprisingly high, and because soap is likely to behave as a competitive inhibitor, substantially lower soap concentrations may cause problems when substrate concentration is low, that is especially during production standstill periods. In addition to its inhibitory effect, soap may cause difficulties in the secondary clarifier, which could not be examined thoroughly in the pilot plant.

On the other hand, the benchmark concentrations retrospectively calculated on the basis of practical experience with the aerated lagoon may be too low, because the substrate

concentration aeration capacity is lower in the lagoon than it will be in the future activated sludge facility. The emergency basin, which can be used to abate the effects of releases to the wastewater plant, was not taken into account either. Therefore, the risks of process units where releases are directed to a wastewater system were apparently overestimated. This was deliberate; it was considered reasonable because the functioning of the wastewater management procedures was not examined closely in this study.

An even greater uncertainty is involved in parameters describing the net loss of a material due to such processes as volatilization, biodegradation and sorption. Although there exist many sophisticated models for describing the influence of external factors on reaction coefficients (Mabey et al. 1982), detailed calculations did not appear reasonable because of the lack of basic data. As winter weather conditions with an ice cover were supposed to prevail in the case of releases straight into the lake system, volatility was considered negligible. Also biodegradation is presumably low in winter, and very low coefficients of overall first order kinetics were utilized.

When a released material is directed to the wastewater treatment plant, weather conditions have only a minor influence on reaction kinetics. Volatilization and degradation are most effective in the aeration basin, but in this case the primary levelling basin is also relevant because it is equipped with aeration devices. Hence, the volatility in the wastewater plant was probably underestimated in this study. Although the net loss rate parameters were uncertain, their effect on the final outcome remained small because of the short retention times. Also in the case of releases to groundwater, the coefficients of reaction kinetics were given very low values. This practice is reasonable because the values can be evaluated more thoroughly, if groundwater effects are found significant in the first rankings.

The results of the index calculations were considered to be reasonable. Even though the uncertainty involved in the results is realistically acknowledged, the relative ranking of the process units with detailed data compiled during the index calculations offers a rational basis for decision making in environmental risk management. Once the data is recorded, the computer program developed in the course of this study can be used for a quick evaluation of the effects of different data or technical options. Environmental risks are closely related to general operational disturbances, and because this method relies on data based on practical operation experience, it can readily be further developed in conjunction with analyses of operational disturbances. Systematic analysis methods of operational disturbances are being developed (Ruuhilehto & Virolainen 1990) and detailed data about disturbances is expected to be available in the future.

## **6.2. Problems and limitations of the index method**

Every risk assessment is pursuit of estimates for uncertain events. The element of uncertainty is inherent in both components of risk estimates: probability of occurrence and magnitude of consequences. The method developed in this study produces a deterministic ranking order of process units without any estimate of uncertainty. This is by no means a unique property belonging to this method only; on the contrary it is typical to risk analysis methods that they produce point estimates rather than probability distributions. Furthermore, it should be clear that uncertainty is not a crucial concern, as no absolute risk estimates but only a ranking order of process units is aimed at.

Although no implicit uncertainty estimate is included in the index developed, uncertainty can be treated in a simple way: by repeating the assessment, varying parameter estimates within their presumed ranges. Because this kind of an uncertainty evaluation is laborious, its applicability in practice is admittedly limited to only a few critical parameters and process units.

The weight of factors involving operation practices is quite low in the present form of this method and it should obviously be upgraded. Like Guymer et al. (1987) have emphasized, to achieve realistic estimates of risk, the role of the operational personnel should be well established. The essential problem is, anyway, how to determine the scores for these factors in practice. An assessment of factors related to personnel attitudes or skill level is difficult to formulate. It is evident that all formal procedures are bound to give deficient results, but if more creative procedures are incorporated, the liability to interevaluator errors increases.

A major problem in an attempt at converting all the environmental risks of a process unit into a single figure is the requirement for the evaluator to estimate the release quantity. As it was pointed out in chapter 3.1.3, the material quantity used in the index represents an expectation value of releases with less than once a year occurrence. An assessment of release quantity implies that the evaluator should define the density function of the releases and to calculate integration over that. Furthermore, the effect of diminishing factors must be incorporated into the quantity term.

## **6.3. Restrictions on the use of the index**

An uncritical use of fixed risk assessment schemes for ranking process units may cause

more harm than benefit. This is because the result of the assessment, the classification, is often blindly accepted as scientifically well justified. The risk assessment method presented here is designed for qualified experts who have the capability to use it as an iterative tool for ranking various process units or production facilities.

It must be emphasized that this method should only be used for a relative ranking of the process units within one site. Although it may be intuitively appealing to incorporate the specific indices related to one process unit into an index value representing the site as a whole, that kind of a practice involves a potential for misuse. If comparisons between various sites are desired, the effect of errors arising from the differences in environmental conditions between the sites must be carefully evaluated. Also the effect of the possible interassessor uncertainty or different production systems must be regarded. The value of the site specific index depends on the process units selected for the index calculations and also on the definition of each unit. Site specific indices can, anyhow, be produced, but the calculations must be made by experts familiar with all the sites to be compared. Therefore, the application of site specific index values should be limited to the internal use of industrial or insurance companies.

#### **6.4. Applicability to other fields**

Although the method was developed especially for pulp and paper industry, the possibility of applying it in other fields was considered already during the development stage. In principle, all production involves material transportation, unloading and loading operations, storing, processing and treatment of residues. In practice, there are substantial differences in the complexity of the processes and in the properties of the materials handled.

It is evident that the processes for example in chemical industry are more varied than those in pulp and paper industry, but this should not mean crucial obstacles for the application of this model, because it centres on quite detailed features rather than on total processes. In addition, some factors used in defining the probability and quantity terms are relatively open-ended, leaving room for evaluators' creativity.

Although the processes of chemical industry are more varied, assessments of risks may be easier there because the material containment is more sharply defined. In pulp and paper industry, the material flows are so high that disturbances in one part of a pro-

duction facility often causes overflows in other parts. Because of the quantity of materials, it is seldom possible to direct the overflows to a containment, and they are typically discharged into wastewater systems.

In addition to chemical process industry, this index system should be readily applicable to operations consisting of transfer and storing of materials. This should comprise the main part of industrial activities. The submodels can be used for impact assessments also where the probability scoring system were proved unfit. The limited accuracy of the submodels must be accounted for, however.

### **6.5. Needs for further development of the method**

There are several distinct route options along which to proceed in the attempts at introducing more reliability, cost effectiveness and applicability of the method. First, in addition to the suggestions presented in chapter 5.2, the probability term scoring system can be further refined through more extensive critical evaluations and practical tests. Especially the operator related factors should receive more emphasis in the probability term.

One possible way of refining the operator related factors is to collect and examine more data on past releases or near misses. Another possibility would be to make parallel assessments using special methods, e.g. the Human Error Analysis. Basically a qualitative method, the HEA alone is not sufficient when an accident is caused by sequential equipment failures or human errors. In such cases, quantitative estimates can be obtained by means of the Fault Tree Analysis, which is a widely used tool for decomposing accidents into sequential contributing factors. General descriptions of the Human Error Analysis and the Fault Tree Analysis are given by AICHE (1985) and Salo et al.(1983).

To mitigate the problems related to determining the release quantity and to diminish the uncertainty of the results, a computerized integration routine can be inserted to the model. Because the extreme values of the discharge quantity distribution can be relatively reliably determined, the most difficult task in gathering data would be to approximate the shape of the distribution. Furthermore, the factors diminishing the discharged quantity could be incorporated, to produce the distribution of release quantity. When the distribution is available, also the uncertainty involved in the impact term can be evaluated.

The practical management of probability distributions is not achievable by means of analytic solutions, instead the stochastic Monte Carlo simulations or deterministic approximations must be used. The Monte Carlo simulation (Hammersley & Handscomb 1979)



is often applied in evaluating the uncertainty of exposure assessments, but it is computationally intensive and possibly not suitable for routine ranking procedures.

As an alternative to the Monte Carlo simulations, Smith & Charbeneau (1990) have tested a first-order uncertainty analysis in groundwater contamination assessments. The analysis linearizes a given function by taking the first two terms of the Taylor series of the input parameter's mean, after which it calculates the mean and variance of the output, drawing upon a simple relation between a linear function of a random variable and the function's mean and variance. Both these analysis methods should be carefully evaluated as alternatives for handling uncertainty in the index system discussed here.

To facilitate model usage, one possibility is to create a database where a microcomputer implement could receive the set of chemical parameters needed in the model. For example, the Natural Resource Damage Assessment Model includes chemical, biological and economic databases, out of which the chemical database comprises over 450 substances (Reed et al. 1989). As regards pulp and paper industry, the assortment of chemicals and process fluids is limited, yet data on them is difficult to gather.

Although the number of chemicals and process fluids used in various facilities is limited, the quality may vary considerably. Also within one facility, many materials exist in differing concentrations. And even if the characteristics of the materials were determined accurately, the environments of the sites studied are never alike and they may have a substantial effect on critical concentrations, for example on the toxicity to activated sludge or water organisms. The database could have implicit algorithms to modify the critical concentrations when critical environmental parameters are introduced to the computer.

The submodels for calculating the concentrations in recipients and biological effects, are simple and give only a rough estimate of reality. Because the index system has a composite structure, these submodels can be easily substituted with more sophisticated ones, when necessary. It must, however, be kept in mind that even though the more complicated models reflect better the actual phenomena in nature, the results may contain an even greater extent of uncertainty when only poor data is available. Experts' views on the optimal structure and performance of environmental models may also vary considerably. When Morgan et al. (1985) compared the models suggested by the leading U.S. scientists for assessing the health effects of a coal-fired power plant, they recognized fundamental differences in the results. Instead of introducing new parameters, a more reasonable way of reducing uncertainty in concentration estimates may be to measure the environmental parameters required in a model, to assure a better adjustment of the model to the specific conditions of the site concerned.

## 7. Conclusions

An environmental risk analysis should in its first phase evaluate potential environmental hazards at plant level. For large process plants, the time consumption hinders the use of conventional quantitative risk analysis methods. Methods for plant-level hazard identification and evaluation are more suitable, because they are quicker and the outcome is a total risk survey for the plant in question. Methods for assessing fire and explosion risks at plant level do exist but no such methods have previously been described for an environmental risk assessment.

Although all risk analyses consist of the same basic components, an environmental analysis should contain unique features to effectively achieve its objectives. The most important special characteristics of environmental risk analyses are considerations of long-term effects from persistent compounds or from gradual releases to soil and groundwater. While many potential environmental damages with negligible immediate economic losses are omitted in safety or economic risk analyses, an environmental risk analysis should carefully study even traditionally unpriced and possibly neglected values.

Therefore, a sophisticated environmental risk analysis technique should include a coarse brushing of potential release scenarios including an adherent probability evaluation but a detailed treatment of the possible environmental and social effects. The index system, developed in this study is an attempt to fulfill these requirements. The method is intended for a preliminary semiquantitative evaluation of environmental risks posed by defined operation systems. The results of its first applications suggest that in many instances no other risk assessments are needed for subsequent decision making.

Pulp and paper production is a capital dominated field, and large scale process or equipment modifications are possible only in the context of plant renewal. The results of this investigation suggest that environmental risks related to accidental releases of hazardous materials in pulp and paper industry are largely associated with a limited number of technical details and operational practices. When this fact is recognized, the environmental risk index appears as an effective device for ranking process units and

allocating environmental risk management resources.

The most frequent causes of accidental hazardous materials releases in pulp and paper industry are related to liquid transfers. Typical causative events are system overflows, unintentional or accidental openings of valves, emptyings of a system for washing or maintenance, ruptures of pipes or hoses etc. Chemical reactions are not likely to cause remarkable accidental releases.

When liquified toxic gases such as chlorine and sulphur dioxide are excluded, it is evident that accidents resulting in catastrophic environmental damages are not possible. Also, excluding licenced emissions like the AOX, the materials and chemicals used are typically not persistent, and long-term effects are related to chemicals used in the manufacturing of by-products. On the other hand, accidents causing smaller scale environmental damages are frequent in this field. In addition to direct environmental effects, these accidents may invalidate efforts to diminish the pollution load of normal operation conditions. In most cases also disturbances to the production and resultant economic losses are substantial. Therefore, environmental risk management is closely related to pollution abatement and to production reliability development.

When sophisticated pollution abatement systems with high capital and running costs are taken into practice, the efficient operation of these systems should be confirmed. There is an obvious need for more detailed data concerning the effects of process fluids and chemicals on the performance of these systems. The environmental risk index model, though hindered by inaccurate data supplies, serves as practical guidance also for research in that field.

In spite of the satisfactory overall behaviour of the index, it should be emphasized that this work was limited by the constraints of time and resources. The method should therefore be further tested and refined. The most critical error sources are related to the assessment of release quantities and valid data on environmental characteristics. The transport and dispersion models of the index were simple and give only a rough estimate of the complicated phenomena occurring in reality. Judging from the experiences of this study, possible errors in the determination of environmental concentration are not of great importance because the final results are only weakly dependent on magnitude of instantaneous releases. In addition, errors in release quantities and environmental parameters involve substantially greater inaccuracy in the assessment of impact magnitude. The use of more detailed models might also result in a so-called information paradox: a more complicated structure of a model leads to an increased uncertainty due to the high number of uncertain parameters.

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Esko Rossi

## Selostus

Puunjalostusteollisuuden ympäristöriskien arviointi edellyttää sekä tuotantoon liittyvien teknisten järjestelmien, toimintatapojen ja päästöjen käsittelyjärjestelmien että ympäristön ominaisuuksien tarkastelua. Näiden kaikkien tekijöiden yhdistäminen yksityiskohtaisten syy-seuraussuhteita jäljittelevän mallin avulla ei ole käytännössä mahdollista. Tässä tutkimuksessa muodostettiin indeksimenetelmä, joka koostuu eri tyyppisistä osamalleista siten, että osamalleja voidaan tarpeen mukaan muuttaa tai korvata uusilla. Menetelmän tavoitteena on antaa mahdollisuus nopeaan ja järjestelmälliseen ympäristöriskien arviointiin toimipaikkatasolla. Toiminnot jaetaan osakokonaisuuksiin eli prosessiyksiköihin, joille lasketaan ympäristöriskin suuruutta kuvaava pistearvo.

Tutkimuksessa tarkasteltiin lyhytaikaisia satunnaispäästöjä ilmaan ja pintaveteen sekä pohjavesevaikutusten osalta myös vähittäisiä pitkään jatkuvia päästöjä. Päästön todennäköisyyden arviointia sekä todennäköisyyteen vaikuttavien järjestelmän ominaispiirteiden tunnistamista varten kehitettiin painotettuun tarkistuslistaan perustuva osamalli. Ympäristövaikutusten laskennassa käytettävän päästön määrän arviointia varten kehitettiin systemaattinen, mutta asiantuntija-arviointiin perustuva menettely.

Päästön leviämisen ja ympäristöön muodostuvien pitoisuuksien laskentaa varten muodostettiin yksinkertaiset laskentamallit ilmaan, pintaveteen ja pohjaveteen kohdistuville päästöille. Leviämislaskelmat muodostettiin pohjavettä lukuunottamatta lyhytaikaisia satunnaispäästöjä varten. Maaperään joutuvien päästöjen pohjavesevaikutusten laskentaan kehitettiin sekä lyhytaikaisia että vähittäisiä pitkään jatkuvia päästöjä käsittelevät mallit.

Leviämislaskelmien tuloksena saatavien pitoisuuksien tai pitoisuusvyöhykkeiden edustamien ympäristövaikutusten laskentaan kehitettiin yksinkertaiset vaikutusfunktiot. Vaikutusfunktiot kehitettiin akuuttien ihmisen terveyteen kohdistuvien vaikutusten, viihtyvyyshaitan, myrkyllisten ja pintakalvon muodostavien aineiden pintavesivaikutusten sekä talousveden käyttöön kohdistuvien vaikutusten laskentaa varten. Vaikutusfunktioiden tuloksena saadaan ennalta määritellyn ympäristöelementin vaurioitumisastetta kuvaava suhdeluku.

Vaikutusfunktioiden tulosten käyttäminen kuviteltuun vahinkotapahtumaan liittyvän riskin suuruuden arviointiin edellyttää funktioiden edustamien kohteiden arvottamista. Ympäristövaikutusten arviointimenetelmäksi valittiin Delphi-menetelmä, joka on joustava ja antaa parhaan mahdollisen tuloksen, jos arviointiryhmä sekä tapahtumakuvaukset on pystytty muodostamaan tilannekohtaisesti oikein.

Menetelmää testattiin suomalaisessa metsäteollisuusintegraatissa. Indeksilaskelmat tehtiin 34:lle prosessiyksikölle, jotka valittiin alustavan riskikartoituksen perusteella. Todennäköisyyskijät määritettiin työryhmäkokouksissa, joihin osallistui tehtaan henkilökuntaa, vakuutusyhtiön edustajia sekä tämän tutkimuksen tekijä. Laskelmissa käytettiin kokemuseräistä aineistoa, kirjallisuudesta koottuja tietoja, pilot-laitteistolla tehtyjen tutkimusten sekä laboratoriotutkimusten ja maastotarkastelujen tuloksia. Mahdollisten vahinkojen arvottamiseen osallistui 9 asiantuntijan työryhmä, jossa oli metsäteollisuuden, ympäristönsuojelun hallinnon, vakuutusyhtiön ja konsulttiryhmän edustus.

Menetelmän tulosten arvioimiseksi tehtiin herkkyystarkasteluja keskeisillä laskelmissa käytetyillä tekijöillä. Osatekijöiden yhdistämistä testattiin myös vektoritarkasteluun perustuvaa vertailumenetelmää käyttäen. Menetelmän luotettavuutta tarkasteltiin vertaamalla saatuja tuloksia vesi- ja ympäristöpiireiltä koottuun metsäteollisuuden yritysten ilmoittamien satunnaispäästöjen tilastoon. Lisäksi tuloksia verrattiin tutkimuksen kohteena olleiden tehtaiden käyttöpäiväkirjoista koottuun läheltä-piti tilastoon.

Kokemusten mukaan menetelmä on sovellettavissa käytännön toimintaan ja tulokset vaikuttavat luotettavilta. Testausten perusteella menetelmään esitettiin osittaisia parannuksia tarkkuuden lisäämiseksi. Käytännössä ongelmakohtia ovat erityisesti todennäköisen päästömäärän sekä eri aineisiin liittyvien ominaisuuksien määrittäminen. Laskelmiin liittyvien epävarmuustekijöiden hallinnan kehittämiseksi tulisi tutkia esimerkiksi Monte Carlo -simuloinnin tai ensimmäisen asteen lineaarisen epävarmuusanalyysin kytkemistä malliin. Lisäksi tulisi lisätä teollisuuden käyttämien aineiden ympäristökäyttäytymistä ja vaikutuksia kuvaavien ominaisuuksien tutkimusta. Vaikka tässä tutkimuksessa kehitetty menetelmä tarkoitettiin erityisesti metsäteollisuuteen soveltuvaksi, voidaan sitä käyttää myös muilla teollisuuden aloilla.

## List of symbols

The following symbols are used in this paper:

$A_{AI}$	Alexander's A sensitivity indicator (dimensionless)
$A_h$	horizontal project area of nonaqueous contaminant plume ( $L^2$ )
$A_v$	vertical project area of nonaqueous contaminant plume ( $L^2$ )
$A_B$	surface area of basin ( $L^2$ )
$A_s$	surface water area affected by surface slick ( $L^2$ )
$a$	scaling factor in probability term (dimensionless)
$b$	slope parameter in equation 24 (dimensionless)
$B_{Be}$	Beimborn's B sensitivity indicator (dimensionless)
BCF	bioconcentration potential factor (dimensionless)
$BOD_7$	biological oxygen demand in 7 days' incubation ( $ML^{-3}$ )
$B_p$	boiling point ( $^{\circ}C$ )
$C_{aH}$	benchmark concentration of airborne acute health effects model ( $ML^{-3}$ )
$C_{AL}$	benchmark concentration of aquatic life effect model ( $ML^{-3}$ )
$C_{g_w}$	contaminant concentration in groundwater supply well ( $ML^{-3}$ )
$C_{g_D}$	contaminant concentration in discharged groundwater ( $ML^{-3}$ )
$C_i$	maximum concentration in basin i ( $ML^{-3}$ )
$C_{ik}$	contaminant concentration in basin i at time $k \cdot \Delta t$ ( $ML^{-3}$ )
$C_0$	initial concentration ( $ML^{-3}$ )
$c(t)$	contaminant concentration at time t ( $ML^{-3}$ )
$C_{i_k}$	contaminant concentration in influent to basin i at time $k \cdot \Delta t$ ( $ML^{-3}$ )
$C_{Dw}$	drinking water standard ( $ML^{-3}$ )
$C_{S_{Dw}}$	contaminant concentration in a surface water body at the point of water intake ( $ML^{-3}$ )
$C_{g_{max}}$	maximum dissolved concentration of contaminant in groundwater ( $ML^{-3}$ )
$cf$	credit factor in probability term (dimensionless)
$d$	threshold thickness for surface slick (L)
$D_L$	longitudinal dispersion coefficient ( $L^2T^{-1}$ )
$D_{aH}$	distance from release point to outer boundary of specified health hazard zone (L)
$E$	exposure ( $ML^{-3}T$ )
$EF_{AH}$	magnitude of health effect of airborne toxics (dimensionless)

$EF_{AL}$	magnitude of effect on aquatic life (dimensionless)
$EF_{AN}$	magnitude of nuisance effect of airborne release (dimensionless)
$EF_{Dw}$	magnitude of effect on drinking water intake from a surface water body (dimensionless)
$EF_s$	magnitude of effect on surface water body from surface slick (dimensionless)
EC50	effective concentration at which the active sludge oxygen consumption is 50 % of control values ( $ML^{-3}$ )
$f(m)$	probability density function of limited discharge quantity (dimensionless)
$f(g)$	probability density function matching the distribution of unlimited discharge quantity (dimensionless)
$F(m)$	distribution function of discharge quantity (dimensionless)
I	net (rain)water infiltration rate ( $LT^{-1}$ )
gf	general penalty factor in probability term (dimensionless)
IDLH	airborne contaminant concentration immediately dangerous to life and health ( $MM^{-1}$ )
k	net-loss rate coefficient ( $T^{-1}$ )
$k_s$	first order decay rate in upper unsaturated zone ( $T^{-1}$ )
$k_R$	first order decay rate in lower unsaturated zone ( $T^{-1}$ )
LC50 <sub>t</sub>	lethal concentration at which 50% of test organisms die within specified exposure duration t ( $ML^{-3}$ )
M	expected release quantity (M)
mm	minimum discharge quantity considered in this study (M)
Ma	mass of contaminant released to air pathway (M)
Mg	mass of release to groundwater pathway (M)
$Mg_d$	contaminant mass discharged from groundwater system (M)
$Mg_{deg}$	contaminant mass degraded in groundwater system (M)
$Mg_Z$	mass of contaminant in unsaturated zone at depth Z (M)
$Mg_s$	mass of contaminant at lower boundary of biologically active unsaturated zone (M)
$Mg_R$	mass of contaminant at lower boundary of unsaturated zone (M)
$M_{max}$	theoretical maximum quantity of release (M)
$M_F$	maximum foreseeable quantity of release (M)
Ms	mass of contaminant released to surface water pathway (M)
Mw	molecular weight (dimensionless)
N	number of alternatives (=process units) (dimensionless)
P	probability term in index system (dimensionless)
$P_{ij}$	probability term for release of material j from process unit i (dimensionless)
$p_o$	probability of occurrence of a discharge ( $T^{-1}$ )
PRS	contaminant persistence factor (dimensionless)
Q	relation of calculated concentration to benchmark concentration (dimensionless)



$Q_A$	aquifer discharge rate used in dilution calculation ( $L^3T^{-1}$ )
$Q_{DW}$	rate of discharge from groundwater supply well ( $L^3T^{-1}$ )
$Q_{AL}$	quotient relating surface water contaminant concentration to aquatic life benchmark concentration ( $ML^{-3}$ )
$Q_{i1}$	contaminated inflow to surface water basin i ( $L^3T^{-1}$ )
$Q_{2i}$	uncontaminated inflow to surface water basin i ( $L^3T^{-1}$ )
$Q_w$	wastewater flow ( $L^3T^{-1}$ )
$R$	contaminant retardation factor (dimensionless)
$RI_i$	risk index for process unit i (dimensionless)
$S$	concentration rate-of-change caused by nonhydraulic physical, chemical and biological processes ( $ML^{-3}T^{-1}$ )
$S_{CHR}$	scaling factor in long-term effects submodel (dimensionless)
$S_{AH}$	downwind health hazard distance (L)
$S_g$	liquid specific gravity relative to water (dimensionless)
$sf$	special penalty factor in probability term (dimensionless)
$t$	exposure time (T)
$\Delta t$	time step in dilution calculation models (T)
$TX_{CHR}$	chronic toxicity factor (dimensionless)
$u$	flow velocity in direction x ( $LT^{-1}$ )
$V_p$	vapour pressure (mm Hg)
$V_E$	contaminant movement velocity in unsaturated zone ( $LT^{-1}$ )
$v_{gw}$	average groundwater velocity ( $LT^{-1}$ )
$V_i$	effective dilutive volume in surface water basin i ( $L^3$ )
$V_{CHR}$	valued long-term effects (dimensionless)
$V_{CHRij}$	impact value from long-term effects from release of material j from process unit i (dimensionless)
$V_{a_{ij}}$	impact value for airborne effects from release of material j from process unit i (dimensionless)
$V_{s_{ij}}$	impact value for surface waters borne effects from release of material j from process unit i (dimensionless)
$VI_{g_{ij}}$	impact value resulting from instantaneous release of material j to groundwater from process unit i (dimensionless)
$VC_{g_{ij}}$	impact value resulting from continuous release of material j to groundwater from process unit i (dimensionless)
$x$	longitudinal distance in river system (L)
$Z$	depth from soil surface (L)
$Z_s$	depth of biologically active soil layer (L)

$Z_R$	depth to groundwater table (L)
$x_{ij}$	rank of alternative (process unit) i with variable at previous value j (dimensionless)
$x_{ik}$	rank of alternative i with variable at changed value k (dimensionless)
$\theta$	volumetric soil moisture content ( $L^3L^{-3}$ )
$\rho$	specific gravity of surface slick material ( $ML^{-3}$ )

## References

- AICHE, 1985: Guidelines for hazard evaluation procedures. American Institute of Chemical Engineers. 180 p. New York.
- AICHE, 1987: Fire & explosion index hazard classification guide. 6th edition. American Institute of Chemical Engineers. 74 p. New York.
- Alexander, E. 1989: Sensitivity analysis in complex decision models. - APA Journal, summer 1989: 323-333.
- Amson, J. 1982: Economic effects. -In: Bennet, G., Feates, F. & Wilder, I. (eds), Hazardous materials spills handbook. p. 23/4 - 39/4. New York.
- Andreasen, P. & Rasmussen, B. 1990: Comparison of methods of hazard identification at plant level. - J. Loss Prev. Process Ind. 3: 339-344.
- Barnthouse, L., DeAngelis, D., Gardner, R., O'Neill, R., Powers, C., Suter II, G., Vaughan, D. 1982: Methodology for environmental risk analysis. -ORNL/TM-8167. Oak Ridge National Laboratory, Oak Ridge, Tennessee. 78 p.
- Benz, J. 1985: A modelling attempt for estimating ecotoxicity. - Environmental modelling for priority setting among existing chemicals. Workshop 11. - 13. Nov. 1985. München-Neuherberg. p. 354 - 370.
- Bernath, T. 1988: Environmental audit and property liability assessment. - Pollution Engineering. Sept. 1988: 110 - 114.
- Borden, R. & Bedient, P. 1986: Transport of dissolved hydrocarbons influenced by oxygen-limited biodegradation. 1. Theoretical development. Wat. Resources Res. 22: 1973-1982.
- Borden, R., Bedient, P., Lee, M., Ward, C. & Wilson, J. 1986: Transport of dissolved hydrocarbons influenced by oxygen-limited biodegradation. 2. Field application. - Wat. Resources Res. 22: 1983-1990.
- Budd, W. 1986: A comparison of three risk assessment techniques for evaluating a hazardous waste landfill. - Haz. Waste & Haz. Mat. 3: 309 - 320.
- Bury, K. 1975: Statistical models in applied science. 625 p. New York.
- Canter, L. 1977: Environmental impact assessment. 331 p. New York.
- Cassidy, K. 1989: CIMAH and the environment - technical problems in assessing environmental risks. - Workshop on Major Hazards, the Preparation of Safety Reports. York, U.K. 8-10 March 1989. IBM Technical Services Ltd. 11 p.
- Cooke, R. & Goossens, L. 1990: The accident sequence precursor methodology for the European Post-Seveso era. - Reliab. Eng. Syst. Safety 27: 117-130.
- Cotruvo, J. 1989: Drinking water standards and risk assessment. - J.IWEM 1989, 3:6 - 12.
- Cuddeback, J. 1989: Assessments, audits and analysis. - Pollution Engineering 21(9): 86-90.
- Dalkey, N. & Helmer, O. 1963: An experimental application of the Delphi method to the use of experts. - Manag. Science 9: 458-467.
- Davies, P. 1989: Major Hazards: Introduction, history & future look. - Workshop on Major Hazards, the Preparation of Safety Reports. York, U.K. 8 - 10 March 1989. IBM Technical Services Ltd. 6 p. + app. 10 p.
- Deelen van, C. 1986: Assessing the risk of soil contamination in the case of industrial activities. -In. Assink, J. & van den Brink, W. (eds), Contaminated Soil. p. 431-440. Dordrecht.

- Deelen van, C. 1989: Methods for assessing the risk of environmental contamination. - In: Seip,H. & Heiberg,A. (eds), Risk management of chemicals in the environment. NATO Challenges of Modern Society. Vol.12. p. 37 - 59. New York.
- EPA 1988: Review of the superfund hazard ranking system. United States Environmental Protection Agency. Office of the Administrator Science Advisory Board-SAB-EC-88-0. 22 p. + app. 78 p. Washington D.C.
- Ettala, J. 1989: Estimating financial loss from fire and explosion accidents on processplants. A master's thesis. Loughborough University of Technology. 143 p. Loughborough.
- Ettala, M. 1988: Application of environmental risk analysis to groundwater protection. - Wat. Sci. Tech. 20:87 -93.
- Falco, J. & Moraski, R. 1989a: Methods used in the United States for the assessment and management of health risk due to chemicals. - In: Seip,H. & Heiberg,A. (eds), Risk management of chemicals in the environment. NATO Challenges of Modern Society. Vol.12. p. 37 - 59. New York.
- Falco, J. & Moraski, R. 1989b: Assessment of ecologic risks related to chemical exposure: Methods and strategies used in the United States. -In: Seip,H, & Heiberg,A. (eds) Risk management of chemicals in the environment. NATO Challenges of Modern Society. Vol. 12. p. 37-59. New York.
- Federal Register 1988: Hazard ranking system (HRS) for uncontrolled hazardous substance releases; Appendix A of the national oil and hazardous substances contingency plan; Proposed rule. Federal Register 53: 51961-52081.
- Frankenberger, W., Emerson, K. & Turner, D. 1989: In situ bioremediation of an underground diesel fuel spill: A case history. - Environ.Manag. 13: 325-332.
- French, D. & French, F. 1989: The biological effects component of the natural resource damage assessment model system. - Oil & Chemical Pollution 5: 125 - 163.
- Genuchten van, M. 1981: Analytical solutions for chemical transport with simultaneous adsorption, zero-order production and first-order decay. - J.Hydrology 49: 213-233.
- Geyer, T., Bellamy, L., Astley, J. & Hurst, N. 1990: Prevent pipe failures due to human errors. - Chemical Engineering Progress. November 1990. p. 66-69
- Grigalunas, T., Opaluch, J. & Tyrell, T. 1989a: The economic damages component of the natural resource damage assessment model system. - Oil & Chemical Pollution 5: 195 - 215.
- Grigalunas, T., Opaluch, J., French, D. & Reed, M. 1989b: Perspective on validating the natural resource damage assessment model system. - Oil & Chemical Pollution 5: 217 - 238.
- Guymer, P., Kaiser, G. & McKelvey, T. 1987: Probabilistic risk assessment in the CPI. - Chem. Eng. Progress 83 (1): 37-45.
- Haith, D. & Laden, E. 1989: Screening of groundwater contaminants by travel-time distributions. - J.Environ Eng. 115: 497 - 512.
- Halfon, E. 1989: Comparison of an index function and a vectorial approach method for ranking waste disposal sites. - Environ. Sci. Tech. 23: 600-609.
- Halfon, E. & Reggiani, M. 1986: On ranking chemicals for environmental hazard. - Environ. Sci. Technol. 20: 1173-1179.
- Halfon, E., Hodson, J.-A. & Miles, K. 1989: An algorithm to plot Hasse diagrams on microcomputers and calcomp plotters. - Ecol. Modelling 47: 189-197.
- Hammersley, J. & Handscomb, D. 1979: Monte Carlo methods. 178 p. London.

- Haus, S. & Wolfinger, T. 1986: Hazard ranking system issue analysis: Review of existing ranking systems. MTR-86W180. The Mitre Corporation, McLean, Virginia. 170 p.
- Heiberg, A. & Hem, K.-G. 1989: Use of formal methods in evaluating countermeasures to coastal water pollution. A case study of the Kristiansand fjord, Southern Norway. - In: Seip, H. & Heiberg, A. (eds), Risk management of chemicals in the environment. NATO Challenges of Modern Society. Vol.12. p.37 - 59. New York.
- Hejde, P., Bachmat, Y., Bredehoeft, J., Andrews, B., Holtz, D. & Sebastian, S. 1985: Groundwater management: the use of numerical models. Water Resources Monograph 5. 43 p. Washington D.C.
- Heinold, D., Smith, D. & Schwab, B. 1988: Evaluating potential impacts from accidental gaseous releases of toxic chemicals. - Environ. Progress 7:116 - 122.
- Hertzman, C., Ostry, A. & Teschke, K. 1989: Environmental risk analysis: A case study. - Can J. Public Health 80: 8-15.
- Hollick, M. 1981: The role of quantitative decision making methods in environmental impact assessment. - J. Environ. Manag. 12: 65-78.
- Hommel, G. 1987: Handbuch der gefährlichen Güter. - Springer Verlag. Berlin.
- ICI, n.d.: Technical manual for Mond fire, explosion & toxicity index. 53 p. + app. 10 p.
- Industry Economics Inc. 1988: Analysis of alternatives to the Superfund hazard ranking system. Final report Vol.V. Industrial Economics Inc., Cambridge, MA. 146 p.
- Jaffe, M. & DiNovo, F. 1987: Local groundwater protection. American Planning Association. Chicago. 234 p.
- Jury, W. 1988: Behaviour of organic contaminants in soil.- In: Wolf, K., van den Brink, W. & Colon, F. (eds) Contaminated soil '88. p. 75 - 82. Kluwer Academic Publishers. Dordrecht.
- Jury, W., Focht, D. & Farmer, W. 1987: Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation. - J. Environ. Qual. 16: 422 - 428.
- Kakko, R. 1990: Vapour cloud modelling in the risk assessment of major toxic hazards- Effect of relative humidity. - Technical Research Centre of Finland. Research Reports 683. 96 p. + app. 26 p. Espoo.
- Kansanen, P., Paasivirta, L. & Väyrynen, T. 1990: Ordination analysis and bioindices based on zoobenthos communities used to assess pollution of a lake in southern Finland. - Hydrobiologia 202: 153-170.
- Katz, W. 1982: Plant operations. In: Bennet, G., Feates, F. & Wilder, I. (eds), Hazardous materials spills handbook. p. 3/6 - 24/6. New York.
- Kayes, P. (ed.) 1985: Manual of industrial hazard assessment techniques. - World Bank. 99 p. + app. 70 p.
- Kemikontoret 1986: Säkerhetsgranskning. En vägledning för skadeförebyggande och skadebegränsande arbete vid industriell kemikaliehantering. Riskhantering 1. 31 p.
- Kletz, T. 198 Eliminating potential process hazards. - Chemical Engineering 92 (7): 46-48.
- Koivisto, R. & Likitalo, A. 1990: Erikoiskemikaalitehtaan turvallisuuksanalyysi (Safety analysis of a specialty chemical plant. Case study) - Kemia-Kemi 17: 22-25.
- Kontaxis, M. & Nusser, J. 1982: Dispersion Modelling. - In: Bennet, G., Feates, F. & Wilder, I. (eds), Hazardous materials spills handbook. p. 23/8 - 29/8. New York.

- Krischok, A., 1988: AGABE - A model for estimating the relative risk of potential contaminated sites. -In: Wolf, K., van den Brink, F. & Colon, F. (eds), Contaminated Soil '88. p. 363 - 365. Kluwer Academic Publishers. Dordrecht.
- Kuijen van, C. 1990: Environmental risk management in the Netherlands. - SRA-Europe Conference: Environmental Risk Management: The European Case. Kiev, 22-24 November 1990. 16 p.
- Kylä-Harakka-Ruonala, T. 1989: Chemicals risk modelling: Toxic effect risk imposed on aquatic organisms by industrial activity. National Board of Waters and the Environment. Publ. Wat. and Environ. Res. Inst. 2: 1-56.
- Landner, L. 1987: Kemiska ämnens miljöfarlighet - manual för inledande bedömning. Slutrapport nr. 1 från projektområdet ESTHER. Naturvårdsverket, Rapport 3243. 100 p. Solna.
- Mabey, W., Smith, J., Podoll, R., Johnson, H., Mill, T., Chou, T.-W., Gates, J., Partridge, I., Jaber, H. & Vandenberg, D. 1982: Aquatic fate process data for organic priority pollutants. - EPA 440/4-81-0114. 434 p. Washington D.C.
- Mackay, D., Roberts, P. & Cherry, J. 1985: Transport of organic contaminants in groundwater. Environ. Sci. Technol. 19: 384 - 392.
- MacKone, T. & Ryan, P. 1989: Human exposures to chemicals through food chains: An uncertainty analysis. - Environ. Sci. Technol. 23: 1154 - 1163.
- Michelsson, P. 1982: Valkaisujätevesien sisältämistä haitallisista aineista ja niiden vaikutuksista vesistöissä (About the toxic components of bleaching waters and their effects in watercourses). - Rep. National Bd Wat. 114: 1-68
- MITRE 1986: Hazard ranking system issue analysis: Toxicity as a ranking factor. Mitre Corporation. MTR-86W128. McLean, Virginia. 118 p. + app. 37 p.
- Montague, D. & Holton, G. 1988: Risk assessment of mixed-waste sites. - IEEE Transactions on Reliability 37: 178 - 191.
- Morgan, G., Henrion, M., Morris, S. & Amaral, D. 1985: Uncertainty in risk assessment. - Environ. Sci. Technol. 19: 662 - 667.
- Mossman, D., Schnoor, J. & Stumm, W. 1988: Predicting the effects of a pesticide release to the Rhine River. - J. Wat. Pollut. Control Fed. 60: 1806-1812.
- Mudan, K. 1989: FIRST, Facility initial risk screening technique. - In: Quantitative risk assessment in the chemical process and related industries. The Center for Professional Advancement. 47 p.
- Murphy, M. 1986: Environmental risk assessment of industrial facilities: Techniques, regulatory initiatives and insurance. - The Sci. Total Environ 51: 185 - 196.
- National Board of Health 1980: Talousveden terveydellisen laadun valvonta (Drinking water quality control). National Board of Health. Circulation No. 1701.
- National Board of Waters and the Environment 1990: Vedet. Kuormitus ja veden laatu (Waters. Load and water quality). - Ympäristökatsaus 8/1990. Helsinki. 2p.
- Nikunen, E., Miettinen, V. & Tulonen, T. 1986: Kemikaalien myrkyllisyys vesieliöille (Toxicity of chemicals to aquatic organisms) Ministry of environment. Publication of the Environmental Protection and Nature Conservation Department D:15/1986. 348 p. Helsinki.
- O'Banion, K. 1980: Use of value functions in environmental decisions. - Environ. Manag. 4: 3-6.
- OECD, 1987: OECD Guidelines for testing of chemicals. 350 p. Paris.
- OECD, 1989: OECD Environmental monographs. No. 27. Compendium of exposure assessment methods for chemicals. 350 p. Paris.
- O'Neill, R., Bartell, S. & Gardner, R. 1983: Patterns of toxicological effects in ecosystems: A modelling study. - Environ. Toxicol. & Chem. 2: 451 - 461.

- Ostendorf, D. 1990: Long term fate and transport of immiscible aviation gasoline in the subsurface environment. - *Wat. Sci. Tech.* 22: 37-44.
- Ott, W. 1978: *Environmental indices. Theory and Practice.* 371 p. Ann Arbor.
- Palmisano, J. & Margolis, J. 1987: Environmental audits as the core of a risk management program. In: *Managing environmental risks.* - Proc. APCA Int. Spec. Conf. Washington D.C., October 1987. p. 61-76.
- Parkhurst, D. 1984: Decision analysis for toxic waste releases. - *J. Environ Manag.* 18: 105-130.
- Pinder, G. & Abriola, L. 1986: On simulation of nonaqueous phase organic compounds in the subsurface. - *Wat. Resources Res.* 22: 109-119.
- Pinter, J., Benedek, P. & Darazs, A. 1990: Risk management of accidental water pollution. An illustrative application. - *Wat. Sci. Tech.* 22: 265-274.
- Pipatti, R. 1989: Teollisuusprosessien suuronnettomuusriskit. (Major hazards in industrial processes. - Technical Research Centre of Finland. Research Reports 584. 155 p. + app. 12 p. Espoo.
- Pipatti, R. & Lautkaski, R. 1987: Vaarallisten aineiden varastointiin liittyvät vaaratilanteet. (Emergencies in storing hazardous materials). - Technical Research Centre of Finland. Research Reports 482. 110 p. + app. 12 p. Espoo.
- Rao, P. 1990: Sorption of organic contaminants. - *Wat.Sci. Tech.* 22: 1-6.
- Reed, M., French, D., Grigalunas, T. & Opaluch, J, 1989: Overview of a natural resource damage assessment model system for coastal and marine environments. - *Oil & Chemical Pollution* 5: 85-97.
- Reible, D., Illangasekare, T., Doshi, D. & Malhiet, M. 1990: Infiltration of immiscible contaminants in the unsaturated zone. - *Ground Water* 28: 685-692.
- Rodricks, J, 1984: Risk assessment at hazardous waste disposal sites. - *Hazardous Waste* 1: 333-362.
- Rosen, B. 1971: *Miljö och miljövård.* 319 p. Borås.
- Rossi, E. 1990: Screening of soil and groundwater contamination risks in an industrial suburban area. - 4th International Conference of Environmental Contamination, Barcelona, Oct. 1990: 306-308.
- Rossi, E. 1991: *Ympäristöindeksi. Käyttäjän käsikirja.* (Environmental risk index. User's Manual). Paavo Ristola Ltd Consulting Engineers. 76 p. + app. 15 p. Hollola. 1990:
- Rouhiainen, V., 1990: The quality assessment of safety analysis. - Technical Research Centre of Finland. Publications 61. 133 p. + app. 30 p. Espoo.
- Rowe, W. 1975: *An anatomy of risk.* 488 p. New York.
- Ruuhilehto, K. & Virolainen, K. 1990: KÄYHÄN! Käyttöhäiriöiden analyysimenetelmä prosessilaitoksen ja sen käytön jatkuvaan kehittämiseen. (IT WORKS! Method to analyze operational disturbances and to improve workperformance at process plants) - Technical Research Centre of Finland. Research Notes 1178. 32 p. Espoo.
- Salo, R. 1990: Kokemuksia riskianalyysien käytöstä. (Experience on the use of Hazard and risk analysis). - *Kemia-Kemi* 17 (1): 19-21.
- Salo, R. Fieandt, J., Himanen, R. & Mankamo, T. 1983: Prosessijärjestelmien riskianalyysi. (Risk analysis of process systems) Technical Research Centre of Finland. Research Notes 171. 118 p. + app. 3 p. Espoo.
- Scott, M. 1987: Applications of risk assessment techniques to hazardous waste management. - *Waste Manag. & Res.* 5: 173-181.
- Schechter, M. 1985: An anatomy of a groundwater contamination episode. - *J. Environ. Econ. Manag.* 12: 72-88.
- Shafer, E. & Davies, J. 1989: Making decisions about environmental management when conventional economic analysis cannot be used. - *Environ. Manag.* 13: 189-197.

- Sierra-Alvarez, R., Kato, M. & Lettinga, G. 1990: The anaerobic biodegradability of paper mill wastewater constituents. - *Environ. Technol.* 11: 891-898.
- Sinden, J. & Worrell, A. 1979: Unpriced values. Decisions without market prices. 511 p. New York.
- Slovic, P. 1987: Perception of risk. - *Science* 236: 280-285.
- Smith, P. & Theberge, J. 1987: Evaluating natural areas using multiple criteria: Theory and practice. - *Environ. Manag.* 11: 447-460.
- Smith, V. & Charbeneau, R. 1990: Probabilistic soil contamination exposure assessment procedures. - *J. Environ. Eng.* 116: 1143-1163.
- Soviet Environmental Protection Committee 1990: Government programme for environment protection and sustainable exploitation of natural resources in USSR for years 1991 - 1995 and forward to year 2005. - *Pravitelstvennyyvestnik*. 40. October 1990.
- Stern, R. 1986: Analysis of the decision making process in chemical safety. - *The Sci. Total Env.* 51: 27 - 62.
- Suokas, J. 1985: On the reliability and validity of safety analysis. - Technical Research Centre of Finland. Publications 25. 69 p. + app. 8 p. Espoo.
- Suter II, G., 1986: Toxicity quotients. In: Barnhouse, L. & Suter II, G. (eds), User's manual for ecological risk assessment. - Oak Ridge National Laboratory. ORNL--6251. p. 31-48. Oak Ridge.
- Suter II, G., Barnhouse, L. & O'Neill, R. 1987: Treatment of risk in environmental impact assessment. - *Environ. Manag.* 11: 295-303.
- Tabakin, R., Trattner, R. & Cheremisinoff, P. 1978: Oil/water separation technology: The options available. - *Water & Sewage Works*. August 1978. p. 72-75.
- Toola, A., Nissilä, M. & Suokas, J. 1990: Automaation vaikutus prosessilaitoksen turvallisuuteen ja luotettavuuteen. (Impact of automation on the safety and reliability of process plants) - *Kemia-Kemi* 17 (1): 26-29.
- Wang, P., Wolfinger, T. & Saari, S. 1987: Hazard ranking system issue analysis: Potential human food chain exposure. - Mitre Corporation, MTR-86W142. 149 p. McLean, Virginia.
- Waldichuk, M. 1985: Methods for measuring the effects of chemicals on aquatic animals as indicators of ecological damage. - In: Vouk, V., Butler, G., Hoel, D. & Peakall, D. (eds), *Methods for estimating risk of chemical injury: Human and nonhuman biota and ecosystems*. Scope 26. p. 493-535. Chichester.
- Verschueren, K. 1983: Handbook of environmental data on organic chemicals. - Van Nostrand Reinhold Company. The Netherlands.
- Whelan, G., Strenge, D., Steelman, B. & Hawley, K. 1985: Development of the remedial action priority system: An improved risk assessment tool for prioritizing hazardous and radioactive-mixed waste disposal sites. - The 6th National Conference on Management of Uncontrolled Hazardous Waste Sites. November 4-6, 1985. p. 432-437. Washington D.C.
- Whyte, A. & Burton, I. (eds) 1980: Environmental risk assessment. SCOPE 15. 157 p. Chichester.
- Volskay, V. & Grady, C. 1988: Toxicity of selected RCRA compounds to activated sludge microorganisms. - *J. Wat. Pollut. Control Fed.* 60: 1850-1856.
- VROM 1983: Guideline soil clean up. Ministry of Housing, Physical Planning and Environment. Hague.



## APPENDIX 1

Analyzed process units with material, probability and release quantity data.

Process unit	Material	Probability data				Migration route	M 10 <sup>3</sup> kg
		gf	sf	cf	P <sub>r</sub>		
<b>Pulp mill/ cooking department</b>							
1. Digester	Black + white liquor	0.50	0.80	0.29	0.05	Wastewater works	55+ 45
2. Washery liquor tank	Weak black liquor	1.35	0.30	0.61	0.12	*	100
3. Turpentine extraction	Turpentine	1.30	0.60	0.72	0.17	*	60kg/h
4. Odour control system	Odorous gases	1.00	2.10	0.68	0.25	Air	
<b>Pulp mill/ chemical department</b>							
5. Green liquor tank	Green liquor	1.65	0.20	0.59	0.13	Wastewater works	100
6. White liquor tank	White liquor	1.15	0.00	0.59	0.08	*	175
7. H <sub>2</sub> SO <sub>4</sub> -tank	H <sub>2</sub> SO <sub>4</sub>	1.15	0.50	0.84	0.17	*	20
8. Erco-reactor +Methanol	H <sub>2</sub> SO <sub>4</sub> +NaClO <sub>3</sub>	1.65	0.60	0.26	0.07	*	35
9. Dreg pit	Leachates				1.00	Soil	9 t/d
<b>Power plant</b>							
10. Black liquor tank (3)	Black liquor	0.50	0.30	0.65	0.06	Wastewater w. rainwater w.	1000+ 1000
11. Soap tank	Black liquor +soaps	1.65	0.20	0.65	0.15	Wastewater w.	50

Process unit	Material	Probability data				Migration route	M 10 <sup>3</sup> kg
		gf	sf	cf	P <sub>r</sub>		
12. Condensate system	Condensates	1.90	0.00	0.65	0.16	"	60t/h
13. Recovery furnace electrofilters	Particles	Experienced			1.00	Air	
<b>Chemical plant</b>							
14. Extraction tanks	Acetone+ Hexane	0.50	0.50	0.34	0.04	Rainwater w.	2.3 (acetone)
15. Soap tank	Soap	1.65	0.00	0.54	0.11	"	200
16. Plant	Acetone+hex. +methanol	Fire	0.001			"	4+8+4
17. Acetone tank	Acetone	1.05	0.30	0.36	0.06	"	10
18. Tall oil tank	Tall oil	1.65	0.90	0.65	0.20	Wastewater w.	200
"	"	Continuous	1.00			+ soil	0.1 kg/d
19. Tank storage	Acetone+hex. +methanol+MEK+ turpentine + tall oil	Fire	0.001			Rainwater w.	40
<b>Paper mill/ chemical department</b>							
20. Glyoxal-tank	Glyoxal(40 %)	1.85	0.20	0.39	0.10	Wastewater w.	35
21. Pastewater system	Pastewater(1%)	2.80	1.00	0.25	0.12	"	60m <sup>3</sup> /h
<b>Paper mill/ paper and coating machines</b>							
22. Pulp tank	Pulp (10%) (10%)	1.55	0.20	0.67	0.14	Wastewater w.	20

Process unit	Material	Probability data				Migration route	M 10 <sup>3</sup> kg
		gf	sf	cf	P <sub>r</sub>		
<b>Paper mill/ grinding department</b>							
23.Sodium hydr. system	NaOH (50 %)	1.95	0.70	0.50	0.16	Wastewater w. Rainwater w.	5 4
<b>Log storage, debarking and chipping</b>							
24.Fuel tank 5m <sup>3</sup>	Diesel oil	1.15	0.30	0.52	0.09	Lake	2
25.Fuel tank 10m <sup>3</sup>	"	1.15	0.30	0.66	0.12	Soil	0.1
26.Crane	Hydr. oil	0.40	1.00	0.62	0.11	Lake	0.1
<b>Plywood mill</b>							
27.Glue mixing	Phenolic resin+ V7F	1.25	0.20	0.59	0.10	Wastewater w.	2+0.15
<b>Sawmill</b>							
28.Impregnation	Sinesto B	1.65	0.00	0.48	0.10	Rainwater w. +soil	0.5 0.2
<b>Central storage</b>							
29.Residual oil tank	Residual oil	1.05	0.00	0.60	0.08	Wastewater w.	2
30.Fuel oil tank	Diesel oil	1.25	0.30	0.32	0.06	" + soil	10 1
<b>Central maintenance</b>							
31.Waste oil tank	Waste oil	1.40	0.00	0.40	0.07	Wastewater w. +soil	0.2 0.5 kg/d

Process unit	Material	Probability data				Migration route	M 10 <sup>3</sup> kg
		gf	sf	cf	P <sub>r</sub>		
<b>Transportation department</b>							
32. Fuel tank	Diesel oil	1.15	0.30	0.66	0.12	Soil	2
<b>Wastewater works</b>							
33. Wastewater works	Wastewater (total S)	Continuous release				Soil	50 t/d
<b>Wastewater treatment plant</b>							
34. H <sub>2</sub> SO <sub>4</sub> tank	H <sub>2</sub> SO <sub>4</sub>	1.65	0.30	0.47	0.11	Wastewater	45