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RISK ASSESSMENT OF CONTAMINATED SITES
CASE STUDY OF A LANDFILL

HODNOCENÍ RIZIK KONTAMINOVANÝCH ÚZEMÍ
PŘÍPADOVÁ STUDIE SKLÁDKY ODPADŮ

DISERTAČNÍ PRÁCE
Ph.D. THESIS

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ABSTRACT

Environmental pollution is nowadays very often discussed topic. The problem has been started in the 19th century with a development of the coal tar industry. Together with increasing environmental pollution the need of assessing and minimizing the pollution appears. Nowadays the environmental risk assessment is a science discipline; this survey is a contribution to this topic.

The survey deals with groundwater contamination and effect of groundwater contamination to surface water. Environmental risk assessment methodology of contaminated sites is being developed here.

Two existing methodologies – RISC 4 and RCR - have been tested to assess risk for groundwater and for surface water. The RISC 4 software has been used for exposure assessment and the RCR (risk characterization ratio) has been calculated for risk characterization.

For the investigation purpose the case study of a landfill was done. The landfill was selected because landfills are according to several studies considered to be one of the highest threats to groundwater. As the case study object an old municipal and industrial landfill in a town Grindsted in Denmark was selected.

The landfill survey is focused on BTEX (benzene, toluene, ethylbenzene, xylenes), chlorinated compounds, and pharmaceutical compounds (sulfoamides and barbiturates). Environmental fate and behaviour have been investigated for all these chemicals. Modelling of their transport in the subsurface has been done; subsequently risk assessment for the groundwater downgradient from the landfill has taken place. Surface water is threatened by groundwater percolation therefore the risk assessment of surface water recipients downgradient from the landfill has been carried out too.

Investigation of pharmaceutical compounds behaviour in the enviromnent is a new approach. It has never been supposed that barbiturates and sulfonamides, which have been developed as drugs, can end up as groundwater pollutants. Very little is known about their fate and behaviour in the environment. This study investigates these chemicals as the environmental pollutants which is really uncommon approach.

KEY WORDS

Risk assessment, environmental risk assessment, groundwater pollution, surface water pollution, landfill, landfill leachate, BTEX, chlorinated compounds, barbiturates, sulphonamides, chemicals environmental fate and transport modelling, chemicals environmental concentrations

ABSTRAKT

Znečištění životního prostředí je v současné době často diskutovaným tématem. Problém se objevil v 19. století zejména s rozvojem zpracování kamenouhelného dehtu. Společně s rostoucím znečištěním životního prostředí vznikla potřeba ono znečištění hodnotit a v neposlední řadě také minimalizovat. V současnosti je environmentální hodnocení rizik vědeckou disciplínou; práce je příspěvkem na toto téma.

Práce se zabývá znečištěním podzemní vody a vlivem tohoto znečištění na vodu povrchovou. Je zde vyvíjena metodika hodnocení rizik pro životní prostředí.

K hodnocení rizik pro podzemní a povrchovou vodu byly testovány dvě existující metodiky - RISC 4 a RCR. Počítačový program RISC 4 byl použit pro hodnocení expozice a RCR (zkratka pochází z anglického - **r**isk **c**haracterization **r**atio = poměr charakterizující riziko) byl užit pro charakterizaci rizika.

Za účelem výzkumu metodiky hodnocení environmentálních rizik byla provedena případová studie skládky odpadů. Skládka odpadů byla vybrána, neboť dle řady studií jsou skládky odpadů považovány za jednu z největších hrozeb pro kvalitu podzemní vody. Předmětem případové studie je skládka komunálního a průmyslového odpadu poblíž města Grindstead v Dánsku.

Výzkum na skládce je zaměřen na BTEX (benzen, toluen, etylbenzen, xyleny), chlorované sloučeniny a farmaceutické látky (sulfonamidy a barbituráty). Pro všechny tyto látky byl zkoumán jejich osud a způsob pohybu v životním prostředí. Bylo provedeno modelování jejich transportu podzemní vodou, následně pak bylo provedeno hodnocení rizik pro podzemní vodu nacházející se ve směru gradientu od skládky. Povrchová voda je ohrožena průsakem podzemní vody, takže bylo provedeno též hodnocení rizik i pro povrchovou vodu nacházející se ve směru toku vody podzemní.

Výzkum chování farmaceutických látek v životním prostředí je novou záležitostí. Nikdy se nepředpokládalo, že barbituráty a sulfonamidy, které byly vyvinuty jako léčiva, mohou kontaminovat životní prostředí. O jejich osudu a pohybu životním prostředím je známo jen velmi málo. Tato studie zkoumá barbituráty a sulfonamidy jakožto polutanty životního prostředí, což je skutečně velmi vzácný přístup.

KLÍČOVÁ SLOVA

Hodnocení rizik, hodnocení rizik pro životní prostředí, environmentální hodnocení rizik, znečištění podzemní vody, znečištění povrchové vody, skládky odpadů, výluh ze skládky odpadů, BTEX, chlorované sloučeniny, barbituráty, sulfonamidy, modelování osudu a transportu chemických látek v životním prostředí, koncentrace chemických látek v životním prostředí

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AUTHOR'S CONFIRMATION

I confirm I am the original author of the thesis. I have compiled the thesis during my study stay at the Technical University of Denmark. I confirm I have compiled it myself using technical literature listed in the references with a supervision of Prof. Ing. František Babinec, CSc. from the Brno University of Technology and Peter Kjeldsen and Anders Baun from the Technical University of Denmark.

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CONTENTS

1. INTRODUCTION

Pollution problem have been started in the 19th century with the production of dyes and other organic chemicals developed from coal tar industry in Germany. During the 20th century the pollution problem increased drastically with production of steel and iron, lead batteries, petroleum refining and other industrial practices. The period of World War II leads in massive production of wartime products which needed a use of chlorinated solvents, polymers, plastics, paints, metal finishing and wood preservatives. Very little was known about the environmental impact of many of these chemicals wastes until much later [8]. Nowadays around 100 000 of chemicals are registered at EU market and more than 1 000 of new chemicals are introduced annually.

This project is focused on groundwater contamination and effect of groundwater contamination to surface water. Aim of the study is to form a methodology of risk assessment of contaminated sites. Several sub steps needed to be investigated to complete the methodology.

First major contribution of the project is summarising of risk assessment itself with a focus on environmental risk assessment. Risk assessment is an engineering process of evaluation of effects of pollution. Information about how to conduct a risk assessment is not easily accessible. The project gathers information about risk assessment history and development and describes how to conduct environmental risk assessment in details.

During the project special chemical data sheet were developed which gathers chemical information necessary for the environmental risk assessment. Structure of these data sheets were designed directly to the purpose of the environmental risk assessment and can be followed (or used in case of environmental risk assessment of the same compounds) for environmental risk assessment generally.

Combination of two methodologies for exposure assessment and risk characterisation was tested to assess risk for groundwater and for surface water which is threatened by contaminated groundwater percolation. For exposure assessment software RISC 4 was used and for risk characterisation a risk characterisation ratio (RCR) was calculated.

Possibilities of RISC 4 software for groundwater risk assessment were tested. This software was developed for human health and surface water (contaminated via groundwater) risk assessment. However the RISC 4 allows modelling of contamination concentration in groundwater in selected distances from the pollution source. The possibility to use the software for groundwater risk assessment was investigated in this project.

Due to program limitations was not possible to model all suspected contaminants together. It was necessary to select representative contaminants which were modelled via the software. Additional contribution of this project is the compound selection methodology which is in details described in the Capture 9.2.

Another contribution of the study is testing of RCR in comparison with water quality criteria. Measured/modelled concentrations were compared with water quality criteria and subsequently RCR was calculated to get knowledge how it match each other. If no water quality criteria for investigated chemical exist the RCR can be used for environmental risk assessing without any problems.

For all upper mentioned investigations a case study of a landfill was done. Why groundwater pollution from a landfill was investigated? According to several studies landfills are considered to be one of the highest threats to groundwater. Conclusions of three studies follow.

In the *National Quality Water Inventory - 1988 Report to Congress* were presented as the most threats to groundwater underground storage tanks, septic tanks, agricultural activities, municipal landfills, and abandoned hazardous waste sites. Other sources also included in the report are industrial landfills, injection wells, regulated hazardous waste sites, land application, road salt, salt water intrusion, and brine pits from oil and gas wells [8]. The Office of Technology and Assessment (OTA) listed in report *Protecting the Nation's Groundwater from Contamination* (1984) more than 30 different potential sources of groundwater contamination. As the most problematic sources have been defined underground storage tanks, abandoned waste sites, agricultural activities, septic tanks, surface impoundments, and municipal landfills [8]. Another study carried out in The Netherlands investigated sources, types, and frequency of soil and subsequently of groundwater contamination from 100 sites. The results are summarized in the Table 1.1. According to this study it is observed that landfills present a quarter of overall frequency of the soil contamination. They are the second most harmful source (after gasworks) of soil and thereafter of groundwater contamination.

Table 1.1 - Classification of types and sources of soil contamination in The Netherlands

Source of contamination	Type of contamination	Frequency (%)
Gasworks	Aromatic hydrocarbons, phenols, CN^-	45
Waste dumps and landfills	Halogenated hydrocarbons, alkyl-benzenes; metals like As, Pb, Cd, Ni, CN^-; pesticides	26
Chemical production and handling sites (including painting industries and tanneries)	Halogenated hydrocarbons, alkyl-benzenes; metals like Pb, Cr, Zn, As	13
Metal plating and cleaning industries	Tri- and tetrachloroethylene, benzene, toluene, Cr, Cd, Zn, CN^-	9
Pesticide manufacturing sites	Pesticides, Hg, As, Cu	4
Automobile service facilities (including gasoline storage tanks)	Hydrocarbons, Pb	3

Source: Practical Handbook of Soil, Vadose Zone and Ground-Water Contamination: Assessment, Prevention, and Remediation - J. Russell Boulding, [12]

A case study of the project is focused on a survey at an old municipal and industrial landfill in a town Grindsted in Denmark respective in Jutland. There was already done a survey by Technical University of Denmark, Institute of Environmental & Resources in 1990ties. Quality of groundwater is very important in Denmark because almost all drinking water is supplied by groundwater. The present survey objective is to broad previous study and carries out risk assessment for groundwater under the landfill and downgradient from the landfill and also for surface water recipients downgradient from the landfill - river and lake.

The study in 1990's was concerned to BTEX investigation; present survey is also focused on BTEX but it is also extended to chlorinated compounds and pharmaceutical compounds investigation. It is supposed that groundwater below the landfill is contaminated by these compounds because a pharmaceutical company disposed its chemical waste here.

Investigation of pharmaceutical compounds respective barbiturates and sulfonamides behaviour in groundwater is a new approach. It has never been supposed that barbiturates and sulfonamides, which have been developed for a use as drugs, can end up as groundwater pollutants. So only few studies concerned to this topic were done. This project investigates behaviour of sulfonamides and barbiturates in the environment – possibilities for biodegradation, accumulation, environmental movement etc. This is a big contribution of sulfonamides and barbiturates investigation as environmental/ groundwater pollutants. On the basis of behaviour in animals/human bodies the environmental fate was investigated. Also modelling of environmental movement via RISC 4 was done. The results are valuable for any other sulfonamides and/or barbiturates environmental pollution investigation.

Practical survey at the landfill was focused on taking of groundwater and soil samples. Five groundwater samples were taken from five different locations (five sampling wells) and five soil samples also from five different locations. Groundwater samples were analyzed for selected compounds – BTEX, chlorinated compounds, sulfonamides and barbiturates. Soil samples were used for leaching tests; the leachates were also analysed for BTEX, chlorinated compounds, sulfonamides and barbiturates. The analysis set concentrations of the contaminants in the groundwater samples and in the leachates. These concentrations were used as an input for contaminants movement modelling via RISC 4 software.

All upper mentioned substeps contribute to a research of groundwater risk assessment methodology. Conclusions of investigated items can be used generally for groundwater contamination movement and/or for groundwater risk assessment as well as chemicals characteristics needed for the groundwater risk assessment.

2. GROUNDWATER POLLUTION

2.1 Introduction to Groundwater Pollution

In general there are two types of groundwater contamination - point sources and nonpoint sources. Point sources are those that release contaminants from a discrete geographic location, including leaking underground storage tanks, and ruptured or corroded transfer pipes (the cause of most fuel leaks), septic systems, and injection wells. Nonpoint sources of contamination are more extensive in area and diffuse in nature. It is therefore difficult to trace contaminants from nonpoint sources back to their origin. Agricultural activities (i.e., application of pesticides and fertilizers), urban run off, and atmospheric deposition are potential nonpoint contamination sources [12].

As the most treating to groundwater have been observed underground storage tanks, municipal and industrial landfills, sewage systems/treatments and septic tanks, and agricultural fields.

Leaking underground storage tanks were found as the second most frequent source of groundwater contamination in both rural and urban areas. Those represent point sources contamination. These are usually old, corroded underground fuel storage tanks. The class of contaminants entering subsurface from these tanks is petroleum-based hydrocarbon fuels. These contaminants are classified according their decreasing volatility as: BTEX (benzene, ethylbenzene, toluene, and total xylenes), total petroleum hydrocarbons as gasoline, and total petroleum hydrocarbons as fuel oil. The biggest number of this underground storage tanks are at fuel storages and retail outlets. But businesses, farms and homes may contribute to this kind of contamination too.

Other significant point sources of groundwater contamination are municipal and industrial landfills. They are considered to be one of the most threatening sources for groundwater. Especially old landfills were built without any impermeable layers so leachating from these landfills to groundwater can occur very easily and present really considerable problem. The contaminants leaching from this source are BTEX, various metals (e.g. Cd, Cr, Cu, Pb, Ni, Zn), cyanide, arsenic, and various synthetic halogenated hydrocarbons and polynuclear aromatic hydrocarbons (e.g. dichlorethans, trichlorethanes, trichloroethylene, tertachloroethylene, chloroform, hexachlorobenzene, polychlorinated biphenyls, and naphtalene) [63].

Sewage systems or treatments and septic tanks are other major category of groundwater pollution. They are also considered to be point sources of contamination. The main pollutants come from this sources are the soluble forms of nitrogen and phosphorous, bacteria and dissolved (or colloidal) organic matter (also called dissolved organic carbon or DOC). Bacteria and phosphorous are usually not a problem for groundwater, except the areas with highly permeable soils, because soil is good filter for bacteria; phosphorous is often limiting nutrient which ensures rapid consumption. DOC can cause an undesirable taste and/or odour but generally is not harmful. Consequently the main problem of sewage systems and septic tanks are nitrates and nitrites.

Agricultural fields also pose a problem for groundwater. Varieties of pesticides are broadly applied on the fields (such as alachlor, atrazine, metalochlor, simazine) and subsequently leaching of them to the groundwater occurs. This represents nonpoint source of pesticides contamination. But there was also found out much higher frequency of pesticides detection in areas close (≤ 0.8 km) to pesticide dealers' sites, producers or applicators - this is point source of pesticides contamination.

The figure below shows the major sources of contamination, both point and nonpiont sources, and possible mechanisms of groundwater contamination.

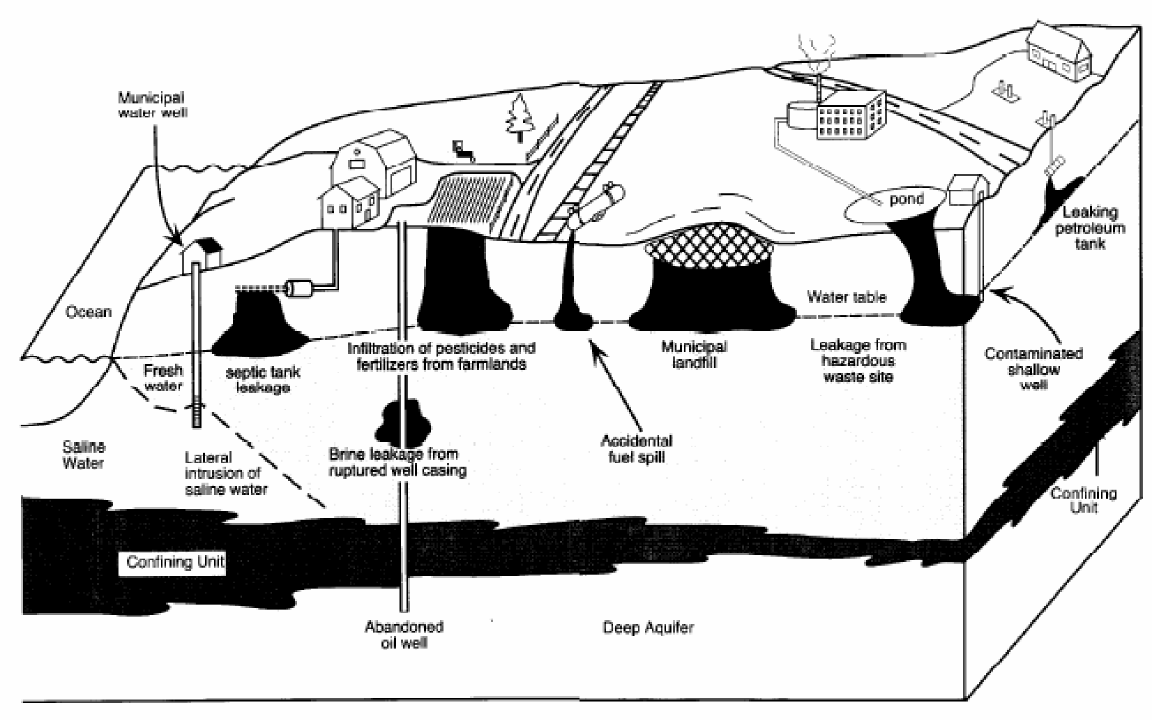


Figure 2.1 - Mechanisms of groundwater contamination [8]

2.2 Contaminant Transport Mechanisms

The extent to which is contaminant spread is governed by physical processes that occur when contaminant enter the groundwater. The main transport processes are advection, and hydrodynamic dispersion. The process which retards the movement of contaminant is called sorption. The main mechanisms of the processes are discussed below.

2.2.1 Advection

Advection is a process when dissolved contaminants are transported together with groundwater in the direction of its flow. The groundwater flow is described by Darcy's law. When advection is the only process governing the movement contaminants are transported together with the groundwater and the transport average velocity is equal to the average linear velocity of the water.

2.2.2 Hydrodynamic Dispersion

Usually advection is not the only one process of contaminant spreading; it is followed by process called hydrodynamic dispersion. Hydrodynamic dispersion is common name for two different processes (molecular) diffusion and (mechanical) dispersion; these processes are effectively inseparable.

Molecular diffusion is a molecular mass transport process in which solutes move from areas of higher concentration to areas of lower concentration [8]. Significance of molecular diffusion is the greatest in the groundwater with low flow velocities or within high concentration gradient. Molecular diffusion may occur even if no motion of groundwater is considered; thus in circumstances of very low permeability or hydraulic gradient movement of contaminant caused by diffusion may approach or exceed velocities of advective transport. Diffusion mass transfer is described by Fick's first law of diffusion:

$$f_x = -D_d \cdot \frac{\partial C}{\partial x}$$ **Equation 2.1**

where: f_x mass flux [kg·m^{-2}·s^{-1}]
D_d diffusion coefficient [m^2·s^{-1}]
dC/d_x concentration gradient [kg·m^{-3}·s^{-1}]

Mechanical dispersion is a mixing process caused by velocity variations in the porous media. Inside the pores there is the highest velocity in the middle of the pore and contaminant can spread there the fastest. Also in the layers of different permeability contaminant spread the fastest within the layers of the highest permeability. Dispersion spread sharp front of contaminant plume. Dispersion is a function of average linear velocity and factor called dispersivity - *α*. There exist three kinds of dispersivity - longitudinal (affect the flow direction), transverse (affect the perpendicular horizontal flow direction), and vertical (affect the perpendicular vertical flow direction). Typical values for longitudinal dispersivity are meters, for transverse decimetres, and for vertical dispersivity millimetres. Mechanical dispersion can be calculated using following equation:

$$D_{x,y,z} = \alpha_{x,y,z} \cdot v_x$$ **Equation 2.2**

where: $D_{x,y,z}$ dispersion coefficient for longitudinal, transvese or vertical dispersion [m^2·s^{-1}]
$\alpha_{x,y,z}$ longitudinal, transvese or vertical dispersivity [m]
v_x average linear velocity [m·s^{-1}]

2.2.3 Sorption

Movement of contaminant within the groundwater can be retard by a mechanism called sorption. In general sorption consists of two mechanisms *adsorption* and *absorption*. Adsorption is the association of contaminant molecules with a surface of solid particle. Absorption is the association of contaminant molecules within a solid particle. Both these processes - adsorption and absorption - may occur simultaneously so sometimes is difficult to decide which of them is taking place. But sorption is common name for both of them. The molecules association is usually temporally and when the contaminant concentration decreases the reverse process - *desorption* - occurs. The ability of contaminant to leach into groundwater is consequently influenced by the extent and rate of sorption. Contaminants of high water solubility tent to be transported by water flow whereas contaminants of low water solubility sorb strongly to soil particles and tend to be spread by diffusion. The major surfaces available for sorption are organic matters and clay. Other parameters such as competitive ions, soil solute concentrations, and pH control the degree of sorption and the amount of desorption significantly.

There exist coefficients which help to express sorption of contaminants in the solid phase. These are - octanol-water partition coefficient K_{ow}, distribution coefficient K_d (also called partition coefficient K_p), and organic carbon partition coefficient K_{oc}.

The tendency of a contaminant to associate with the organic fraction of aquifer solids express *octanol-water partition coefficient* K_{ow}. To set the value of the coefficient two-phase system consists of octanol and water is used. Then the contaminant is added to the system and after equilibrium the concentration of contaminant in both phases is determined and referred to as the octanol-water partition coefficient. The mathematical expression is following:

$$K_{ow} = \frac{C_o}{C_w}$$ **Equation 2.3**

where: C_o concentration of contaminant in octanol [mg·l^{-1}]
C_w concentration of contaminant in water [mg·l^{-1}]
K_{ow} octanol-water partition coefficient [dimensionless, but truly l·l^{-1}]

To express the distribution of contaminants between solid and aqueous phase the *distribution coefficient* K_d (also called *partition coefficient* K_p) is used. It is assumed that the sorption process is a linear relation between concentration of substance in solid phase and concentration of substance in aqueous phase. It is expressed by following equation:

$$C_s = C_w \cdot K_d$$ **Equation 2.4**

where: C_s concentration of substance in solid phase [mg·(kg solid phase)$^{-1}$]
C_w concentration of substance in aqueous phase [mg·(litre water)$^{-1}$]
K_d distribution coefficient between solid phase and water [l·kg^{-1}]

This equation is widely used to describe sorption in soil and aquatic environment.

Another very useful linear coefficient is the *organic carbon partition coefficient* K_{oc}. It describes partitioning between contaminant and natural organic matter. K_d can be also set using this coefficient:

$$K_d = K_{oc} \cdot f_{oc}$$ **Equation 2.5**

where: K_d distribution coefficient [l·kg^{-1}]
K_{oc} organic carbon partition coefficient [l·kg^{-1}]
f_{oc} fraction of organic carbon [-]

Fraction of organic carbon describes the weith of organic matter of the aquifer material. In above equation the sorption of contaminant is a function of the amount of solid phase natural organic matter (fraction of organic carbon) and the relative hydrophobicity of the contamninant itself. Fraction of organic carbon is a site-specific parameter dependent on the character of the soil. While f_{oc} has to be measured, the K_{oc} value could be set on the basis of K_{ow} value. There exist several equations for determining of K_{oc} on the basis of K_{ow} according to the type of pollutant and/or organic carbon content. The most recommended is Abdul's formula:

$$\log K_{oc} = 1.04 \cdot \log K_{ow} - 0.84$$ **Equation 2.6**

It could be used only for pollutants with $K_{ow} > 5$ and solids with $f_{oc} > 0.1\%$.

Or for a rough estimation following equation could be also used.

$$K_{oc} = 0.41 \cdot K_{ow}$$ **Equation 2.7**

The slow of the contaminant movement can be expressed by *retardation factor*. The retardation factor is the ratio between groundwater flow velocity and contaminant migration velocity. Mathematical expression of retardation factor is following:

$$R = 1 + K_d \frac{\rho_b}{n}$$ **Equation 2.8**

where: R retardation factor
K_d distribution coefficient
ρ_b bulk density
n porosity

For example if $R = 10$ it means that the groundwater is moving ten times faster than the contaminant plume.

2.3 Contaminant Fate Processes

Other processes which influenced contaminant fate in the subsurface are degradation (abiotic or biotic) and volatilisation. These processes are discussed bellow.

2.3.1 Abiotic Degradation

These are processes which occur without contribution of living organisms; therefore are called abiotic processes. There were identified several reactions which impact the fate of certain contaminant in groundwater. Among the most important abiotic reactions belong hydrolysis, oxidation-reduction reactions, and elimination reactions. The extent of these reactions is highly compound-specific and is also influenced a lot by local conditions of the site.

2.3.2 Biodegradation

As the name suggest this type of degradation take place under the biotic conditions - via living organisms. Biodegradation is a complete conversion of contaminant to mineralized end products - CO_2, H_2O, and salts. In all groundwater systems live bacteria which are indigenous to the aquifer and through their metabolism the degradation reactions occur. In some cases the metabolism processes do not cause whole mineralization of the substance; however the metabolic activity induces a chemical change. This process is then called *biotransformation*. Via biotransformation harmful contaminants can be transformed to less or not harmful contaminants but in some cases also the opposite way may occur - it means from not so harmful contaminants more harmful or very dangerous contaminants may be tramsformed.

The biodegradation of groundwater contaminants is extremely important fate processes since it can impact the fate of all organic contaminants. This is really complicated process because of bacteria diversity and range of metabolic processes.

One of the most commonly used expressions for biodegradation is first-order decay kinetics. It represents degradation of organic compounds and involves an exponential decay relationship:

$$C = C_0 \cdot e^{-k \cdot t}$$ **Equation 2.9**

where: C biodegraded concentration of the chemical
C_0 starting concentration of the chemical
k rate of decrease of the chemical
t time

The first-order rate constants are often expressed as half-life of the chemical:

$$t_{\frac{1}{2}} = \frac{0.639}{k}$$ **Equation 2.10**

where: $t_{1/2}$ half-life of the chemical
k rate of decrease of the chemical

2.3.3 Volatilization

Volatilization is a process which allows contaminants to transfer from aqueous phase, nonaqueous phase liquid, or sorbed phase directly to the gas phase. The volatilization rate and extent is strongly influenced by parameters such as contaminant phase, contaminant vapour pressure, environmental factors, distance of vadose zone, and other site specific parameters. It is quite complicated to calculate volatilization contribution to the fate of contaminant because of the number of parameters influencing it.

The ability of contaminant to volatile from aqueous solution is described by *Henry's law coefficient* K_H.

$$K_H = \frac{p_a}{S}$$ **Equation 2.11**

where: p_a vapour pressure of the contaminant [atm]
S water solubility of the contaminant [$\mathrm{mol \cdot m^{-3}}$]
K_H Henry's law coefficient [$\mathrm{atm \cdot m^3 \cdot mol^{-1}}$]

There also exists another approach how to set Henry's law coefficient. The approach is similar to above mentioned octanol-water partitioning coefficient; just the two-phase system used is water and air. Contaminant is added to the system and after equilibrium is redressed the concentration of contaminant in both phases is measured. Then the following equation is used to obtain Henry's law coefficient:

$$K_H = \frac{C_a}{C_w}$$ **Equation 2.12**

where: C_a concentration of contaminant in air [$\mathrm{mg \cdot l^{-1}}$]
C_w concentration of contaminant in water [$\mathrm{mg \cdot l^{-1}}$]
K_H Henry's law coefficient [dimensionless]

2.4 Groundwater Pollution from Landfills

2.4.1 Pollution Mechanism

The groundwater contamination from landfills is caused by an infiltration of rainwater through the contaminated soil. The infiltration is the most common way of the groundwater contamination. During precipitation a portion of water percolate from the surface to the subsurface. This water infiltrate slowly to the soil through pore spaces in the soil matrix. As the water moves downward due to the gravity it can dissolve materials which come into the contact with the water. So if it percolates through the contaminated area it can dissolve contaminants and forms leachte (with organic or inorganic constituents) which percolate downward due to the gravity as long as it reaches the saturated zone. The spreading in the saturated zone is influenced by the groundwater flow direction - the leachate moves horizontally in the direction of the groundwater flow and again vertically due to the gravity. The vertical movement occurs until it reaches an impermeable layer.

2.4.2 Landfill Leachate

The landfill leachate is a significant source of groundwater pollution. The leachate is described as a water based solution of compounds from the waste [16]. The landfill leachate is generated by rainwater percolating through waste layers. Combination of physical, chemical, physico-chemical, and microbial processes occurring in the waste transfer pollutants from the waste material to the percolating water.

Among the physical processes belongs dilution; among physico-chemical sorption, and ion exchange; precipitation is characterized as chemical process; and degradation as microbial process.

The landfills leachate may contain four groups of pollutants based on the type of waste (common municipal, commercial, or industrial waste). 1) Dissolve organic matter, expressed as Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC), including CH_4, volatile fatty acids, and more refractory compounds as humic-like compounds. 2) Inorganic macrocomponents: Ca, Mg, Na, K, NH_4^+, Fe, Mn, Cl, SO_4^+, and HCO_3^-. 3) Heavy metals: Cd, Cr, Cu, Pb, Ni, and Zn. 4) Xenobiotic organic compounds (XOCs) originating from household or industrial chemicals and present in relatively low concentrations in the leachate. These compounds include among others a variety of aromatic hydrocarbons, phenols, and chlorinated aliphatic [16].

Leachate composition varies significantly among landfills depending on the waste composition, age of the landfill, and landfill technology. Sampling methods and handling of samples may also influence measured leachate quality. But no standards for leachate smpling, filtration, and storage of samples exist. E.g. heavy metals have strong affinity to colloids so the measured amount of the heavy metals in the leachate sample is strongly dependent on the amount of colloids presented in the sample; volatile compounds may evaporate during sampling procedure so the measurement of them may be biased.

In general the landfill leachate may contain very high concentrations of dissolved organic matter and inorganic macrocomponents. The concentrations of these components may typically be up to a factor 1000 - 5000 higher than groundwater concentration [16]

Several parameters change dramatically as the landfill stabilizes. Initial acid phase is typical by low pH values and high concentrations of many compounds especially high concentrations of easily degradable organic compounds as volatile fatty acids. In later methanogenic phase, when CH_4 production is significant at the landfill, pH increases and the BOD/COD ratio (reflecting the degradability of organic carbon) is lowered dramatically [16].

3. RISK ASSESSMENT

3.1 Introduction to the Risk Assessment

The risk assessment is relatively a new method for decision making at contaminated sites. It started to be taken into account in 1980’s. The risk assessment accounts for surveys at contamination sites, calculations, evaluations, and modelling of contaminants spreading in a site. It combines information on the level of exposure to a substance and its toxicity to characterize what is likely to happen to humans, fauna, flora, and environmental compartments which may be exposed. It is carried out to predict the pollution spreading of contaminated sites and assess a remediation strategy of the sites.

As a contaminated site is considered to be according to the ANZECC (Australian and New Zealand Environment Conservation Council) Guidelines for the Assessment and Management of Contaminated Sites (1992): "A site at which hazardous substances occur at concentrations above background levels and where assessment indicates it poses, or is likely to pose an immediate or long-term hazard to human health or the environment." [44]

Considering to the risk assessment there can be found several definitions in literatures:

- Risk assessment (RA) is a technique by which the actual or potential adverse effects of contaminants on plants, animals, or ecosystem integrity can be assessed in a systematic fashion. Essentially risk assessment asks the question: How likely is it that damage will be or has been done by contaminants? [44]
- Risk assessments are assessments of the environmental and health consequences of a given contamination. The objective of risk assessment is to establish the need for remediation [29].
- Risk assessment is qualitative or quantitative evaluation of the risk posed to human health and/or the environment by the actual or potential presence or release of hazardous substances, pollutants or contaminants. [58]
- Risk assessment is a scientific process in which the risk posed by inherent hazard involved in the process or situations are estimated either quantitatively or qualitatively. Risk assessments are carried out to examine the effect of a substance on humans (Health Risk Assessment) and ecosystems (Environmental Risk Assessment) [40].

Risk assessment is carried out to identify a potential risk and to enable risk management decisions to be made. *Risk management* is the process of identifying, evaluating, selecting, and implementing actions to reduce risk to human health and ecosystem [40]. Another definition says that risk management attempts to reduce the risk that has been discovered through risk assessment [60].

It is quite difficult to find integrated information about risk assessment approach and performing. One of the reasons is that there is a lot of confusion concerning the risk assessment terminology. If you start study risk assessment you will be probably very confused. There is a big ambiguity in the terminology (just the term risk assessment can be also named as risk analysis depending on the document you are using and as far as the other terms are concerned the situation is even worst). However it could be said that in general all documents follow very similar or the same procedure just the constituent steps have different names. Nowadays the situation is that discussions concerning the risk assessment often end up in discussing terminology rather than the risks themselves. More about the terminology problem is published in [17].

The objective of this capture is not to clear all the risk assessment terminology. It is rather focused on description of environmental (ecological) risk assessment conducting. Because sometimes is really difficult to find sufficient and synoptic information about risk assessment in general furthermore about environmental risk assessment. Anyway there is a need to make clear at least two main terms - hazard and risk. *Hazard* is commonly defined as "the potential to cause harm". *Risk* is the combination of the probability, or frequency, of occurrence of a hazard and the magnitude of the consequences of the occurrence [40]. In accordance to these definitions hazard is inseparable attribute of a given substance (e.g. acids may be corrosive and irritant) while the substance can cause risk only if human or environment are exposed to it. The degree of risk is dependent on how hazardous the chemical is and on the amount of exposure too.

Basically there are two types of risk assessment: a human health risk assessment and an ecological risk assessment (also called as an environmental risk assessment). The human health risk assessment evaluates the risk of human exposure to contaminants. The environmental risk assessment is connected to an exposure of flora and/or fauna to contamination. There exists one more type of risk assessment which is not so prominent but not less important than the two mentioned above - it is a building structures risk assessment which deals with a risk posed to building structures due to contact with contamination (e.g. permeation and/or degradation of underground utilities, sewers, building foundations, etc.) [18].

Risk assessment has to consider the whole life-cycle of chemical substances from production to disposal or recovery. The life-cycle covers production, transport and storage, use (large professional use and private or consumer use), waste disposal (including waste treatment, landfill and recovery).

Each risk assessment process is obstructed by several uncertainties. The basic are: lack of or inadequate data, measurement uncertainties (difficulties during measurement, inappropriateness of measurement, human errors), observation conditions (variability in climate, soil type, ecosystem structure, differences between natural and laboratory conditions, differences between tested and observed species), and inadequacies of used models (extrapolations, failure to consider multiple stressors, instability of parameter estimates).

The need or obligation to assess risks is also given by law. In Europe it is SEVESO II Directive. It is adopted in the Czech Republic as law No. 59/2006 Coll., About Serious Accidents.

3.2 History of the Risk Assessment

The risk assessment as a tool for decisions making has been formally introduced in 1980 in the United States via legislating of the *Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)* by the United States Congress. The United States Environmental Protection Agency (U.S. EPA) granted under CERCLA the requirement of human health and environmental risk assessment to be conducted for sites listed on the National Priorities List (Superfund sites). The purpose of the risk assessment was to ensure adequate protection of human health and the environment at Superfund sites [18].

During 1980's several documents and publications have been developed in order to provide guidance for the risk assessment conducting. Even though they provide valuable information only few of them are really useful as guidance how to carry out the risk assessment. In 1989 the U.S. EPA has published a document which deals with this problem and provides guidance for the risk assessment. The document is called *Risk Assessment Guidance for Superfund, Volume I: Human Health Evaluation Manual* and *Volume II: Environmental Evaluation Manual*. As the titles of the manuals suggest the volume I manual provides information how to carry out human risk assessment and the volume II manual provides environmental risk assessment guidance. Especially the *Human health Evaluation Manual* is widely referred as one of the most comprehensive documents published on this topic while the *Environmental Evaluation Manual* provides only basic information about environmental risk assessment.

By 1990 the theory of the risk assessment was becoming common for Superfund sites. In the earlier 1990's some regulatory agencies started to require performing of the risk assessment also for non-Superfund sites especially for leaking underground storage tanks. One of the most important factors for carrying out risk assessment also for non-Superfund sites was a fundamental change of attitude for environmental cleanups [18].

During the 1980's and early 1990's many of government agencies were requiring cleanup of all contaminated sites, regardless of cost. It had resulted to vast expenses of the all environmental cleanups so both government and industry started to seriously question the demand of environmental cleanup at all sites. The new approach for environmental cleanup was to distinguish the sites posing the greatest risk from the sites posing little or no risk. This approach let to develop a consistent decision-making process for the assessment based on protection of human health and the environment. This process is referred to as risk-based corrective action (RBCA) [18].

It could be said that in recent years there is a shift from reactive measures to more proactive approaches aimed at preventing or minimizing of environmental pollution or damage rather than remediation [28].

3.3 Risk Assessment Procedure

The main objective of the risk assessment capture is to provide overall information about risk assessment especially about the environmental risk assessment. It is not an easy task to find brief, sufficient, and synoptic information about neither risk assessment in general nor about environmental risk assessment or human health risk assessment.

As mentioned above in different sources (literatures) it is possible to find different approaches how to conduct the risk assessment. Maybe it is better to say that there are different names given to the risk assessment steps but in general the approaches are very similar or differ only very little. Generally each risk assessment procedure should cover four main steps: (1) data collection and evaluation, (2) exposure assessment, (3) toxicity assessment, (4) risk characterization. This approach is taken from U.S. EPA document *Risk Assessment Guidance for Superfund, Volume I, 1989* [45]. In other documents you can find terms as problem identification for the first step, characterization of exposure for the second step, effect assessment or dose-response relationship for the third step, and risk evaluation for the fourth step. But basically it covers the same actions. In the Figure 3.1 is shown connection between these steps or the process of risk assessment conducting.

Figure 3.1 - Risk assessment procedure

From upper mentioned it is obvious that the risk assessment is a broad topic. It is not the objective of this project to describe the risk assessment procedure in general. The following part of the capture is concerned to the environmental risk assessment and how to conduct the environmental risk assessment.

3.4 Environmental Risk Assessment

3.4.1 Introduction to the Environmental Risk Assessment

In some sources you can find the term environmental risk assessment in another ecological risk assessment - again you can see the problem of ambiguity of terminology - but generally it means the same - an exposure of flora and/or fauna to contamination.

Also for the environmental/ecological risk assessment (commonly used abbreviation is ERA) is possible to find different definitions:

- The environmental risk assessment is a process of predicting whether there may be a risk of adverse effect on an environment caused by chemical substance [20].
- The ecological risk assessment is a qualitative and/or quantitative appraisal of the actual or potential effect of a hazardous waste site on plants and animals other than people or domesticated species [46].
- The ecological risk assessment is a process that evaluates the likelihood that adverse ecological effects are occurring or may occur as a result of exposure to one or more stressors [23].

The ecological risk assessment identifies environmental problems, establishes priorities, and provides a scientific basis for regulatory actions. ERA conducting identifies existing risks or may predict risks of stressors not yet presented in the environment [25].

The expression of ecological risks can be done in different ways. Some ecological risk assessment provides true probabilistic estimates of the adverse effects and exposure elements others may be deterministic or even qualitative in nature. In this case the likelihood of adverse effects is expressed by semiquantitative or quantitative comparison of effects and exposure.

The ecological risk assessment plays an important role in identifying and resolving environmental problems but it is not a solution for all environmental problems nor is it always precondition for an environmental management. In cases of protection of the endangered species or habitats particular statutes or professional judgment are the driving forces in decisions making.

3.4.2 History of the Environmental Risk Assessment

The first published document concerning the environmental risk assessment (and according to accessible information the first at all) has been published by U.S. EPA as the manual mentioned above *Risk Assessment Guidance for Superfund, Volume II: Environmental Evaluation Manual (March 1989)*. This manual contains useful information on the statutory and regulatory basis of ecological assessment, basic ecological concepts, and other background information. Concerning the ecological risk assessment conducting itself it includes only very poor information. There was the need for a document which would include a concept of the ecological risk assessment procedure.

This kind of document has been published in 1992 by U.S. EPA as a *Framework for Ecological Risk Assessment (February 1992)*. This document is mentioned as: “a first step in a long-term program to develop risk assessment guidelines for ecological effects” [25]. It already includes the procedure of the environmental risk assessment conducting. It is possible to say that the procedure follows the general risk assessment procedure as it is described in Capture 3.3 Figure 3.1 (more information about the procedure published in the document are provided in following captures).

The follow-up document published also by U.S. EPA is *Guidelines for Ecological Risk Assessment (April 1998)*. This document expands upon the general procedure of the ecological risk assessment conducting published in the *Framework for Ecological Risk Assessment*.

On the basis of *Proposed Guidelines for Ecological Risk Assessment (August 1996)*, which is only preliminary version of final *Guidelines for Ecological Risk Assessment* published in April 1998, has been published a document *Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessment (U.S. EPA, June 1997)*. This guidance provides process of designing and conducting of technically defensible ecological risk assessment for the Superfund Program.

It promotes consistency and science-based approach of the ecological risk assessment for Superfund. It is based on the two above mentioned documents - *Framework for Ecological Risk Assessment* and *Proposed Guidelines for Ecological Risk Assessment*.

From the above mentioned documents concerning ecological risk assessment conducting the most important are *Framework for Ecological Risk Assessment* and its extension or specification *Guidelines for Ecological Risk Assessment* because they provide general information about ecological risk assessment procedure and conducting. Following captures briefly describe the ecological risk assessment procedure based on these two documents.

3.4.3 Procedure of the Ecological Risk Assessment

The following capture provides basic information about the ecological risk assessment conducting. The described procedure follows the procedure published in the *Framework for Ecological Risk Assessment* with an extension in the *Guidelines for Ecological Risk Assessment*. The term ecological risk assessment is used because in the *Framework* this term is used too.

The *Framework* purpose is to provide basic structure and starting principles for ERA. The ecological risk assessment process described in the *Framework* offers wide latitude for planning and conducting individual risk assessment in many diverse situations. On the basis of the basic principles provided in the *Framework* long-term guidelines for ERA can be organized. However the *Framework* does not include information about substantive guidelines of factors that are integral to the risk assessment process such as analytical methods, techniques for analyzing and interpreting data, or guidance factors influencing policy.

The *Framework* emphasizes three main differences from previous risk assessment approaches. The first one is that ecological risk assessment can consider effects on individuals of single species or may consider whole population, community, or ecosystem impacts. Second difference includes assessment endpoints consideration. In ecological risk assessment there is no general set of assessment endpoints; the endpoints are selected from a very large number of possibilities based on scientific and policy considerations. Finally, to consider the possible effect of non chemical stressors the traditional approach of chemical effect is carried out to ensure a comprehensive ecological risk assessment.

The steps of the ecological risk assessment procedure are shown in the Figure 3.2.

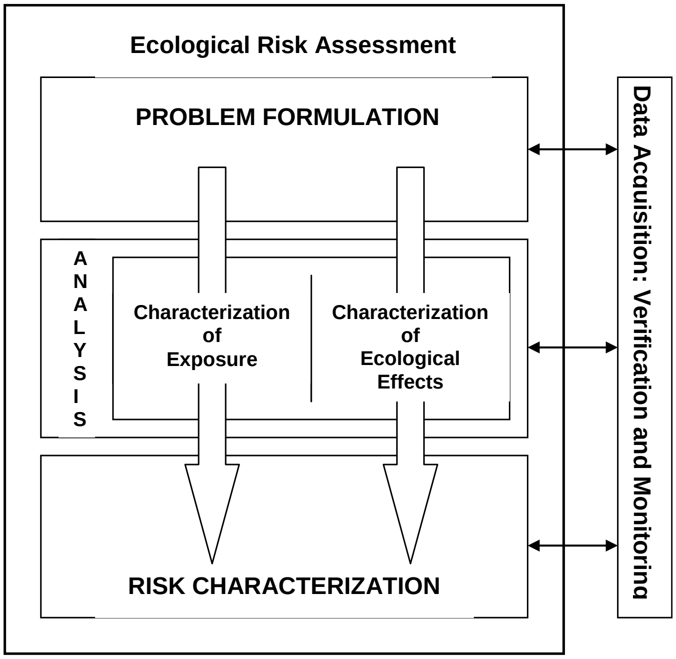


Figure 3.2 - Ecological risk assessment framework [25]

The ecological risk assessment procedure consists of four main steps: (1) problem formulation, (2) characterisation of exposure, (3) characterisation of ecological effects, and (4) risk characterisation. For better overview and to show the connection between each step see the Figure 3.2.

In following text the each step of the ecological risk assessment is described more detailed.

Problem Formulation Phase

As shown in the Figure 3.2 the ecological risk assessment begins with a problem formulation phase. It forms goals, breadth, and focus of the assessment. It is a systematic planning step which defines the key factors to be considered in a particular assessment. The problem formulation phase (see the Figure 3.3) begins with identification and preliminary *characterization of stressors, the ecosystem potentially at risk,* and *ecological effects*. This is an interactive process which contributes to the *endpoint selection*. The endpoint selection may present direct measurement or assessment. The outcome of problem formulation phase is *conceptual model* which describes how the given stressors may affect the ecological compartments in the environment. Conceptual model also covers information about methodologies which will be used to analyze the data.

As *stressors* are considered any physical and chemical entities those can cause adverse effects. Chemical stressors include variety of inorganic and organic substances while physical stressors pose extremes of natural conditions and habitat alteration or destruction. Gathering of these information helps define the ecosystems potentially at risk as well as ecological effects that may results.

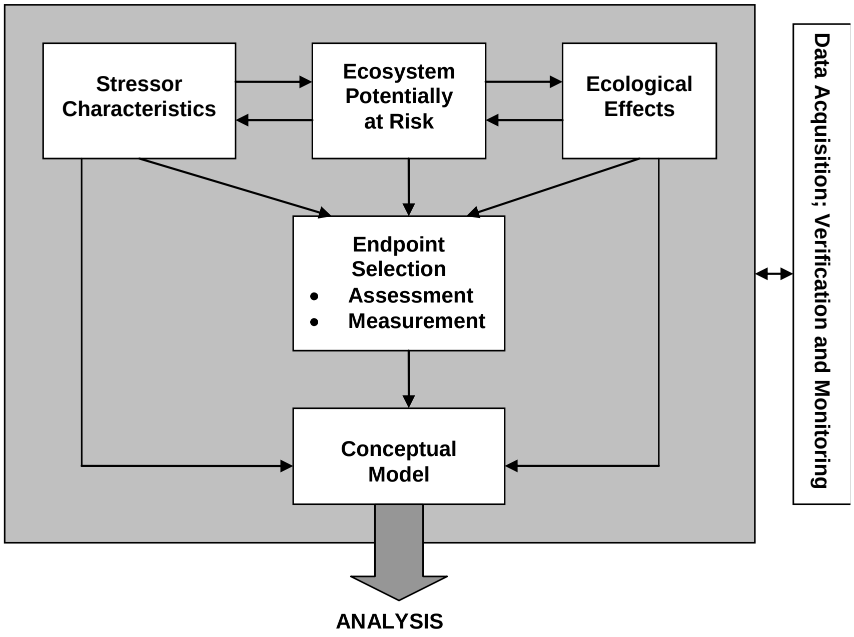


Figure 3.3 - Problem formulation scheme [25]

Knowledge about the *ecosystems potentially at risk* helps identify ecological compartments that can be affected and stressor-ecosystem interaction relevant for exposure scenarios developing. A wide range of ecosystem properties may be considered; among the most relevant belong abiotic environment, ecosystem structure, and ecosystem function. The identification of the ecosystems potentially at risk depends on how the risk assessment was initiated. If firstly the stressor has been identified information about temporal and spatial distribution are needed to set the ecosystems potentially at risk. Oppositely if the risk assessment is initiated by adverse effect observing these effects directly, it identifies the ecosystems or ecological compartments that have to be considered in the assessment.

The data about *ecological effect* may come from a variety of sources. Relevant sources of this information are field observation, field tests, laboratory tests, and chemical structure-activity relationship. Information about stressors can help focus the assessment on specific stressors and on ecological compartments which should be evaluated.

An *endpoint* is a characteristic of an ecological component that may be affected by exposure to a stressor [25]. Assessment of the endpoints is the fundamental focus in the risk characterization. There exist two types of endpoints: (1) assessment endpoints - actual environmental value that has to be protected and (2) measurement endpoints - measurable responses to a stressor that are related to the valued characteristic chosen as the assessment endpoints. If the assessment endpoints can be measured directly the measurement and assessment endpoints are the same. However, usually the assessment endpoint can not be measured directly so the measurement endpoint is selected that can be related to the assessment endpoint qualitatively or quantitatively.

In the *conceptual model* development of exposure scenarios are set. For chemical stressors the exposure scenario usually involves consideration of sources, environmental transport, partitioning of chemical among various environmental media, chemical or biological transformation, and identification of potential exposure routes. Many hypotheses can be generated during the conceptual model development but only these hypotheses that are supposed to most likely contribute to a risk are selected for further evaluation in the next steps. For the chosen hypotheses the approach which is going to be used for the analytical phase, the types of data and analytical tools that will be needed are described in the conceptual model.

Analytical Phase

The analytical phase is based on the conceptual model generated in the problem formulation phase. Although it has two different stages - *characterization of exposure* and *characterization of ecological effect* - it is necessary these two stages proceed simultaneously to ensure that the characterized ecological effects are compatible with the exposure pathways identified in the exposure characterization. For interaction between the two stages see the Figure 3.4. The output of these characterizations is summary profile used in the risk characterisation phase.

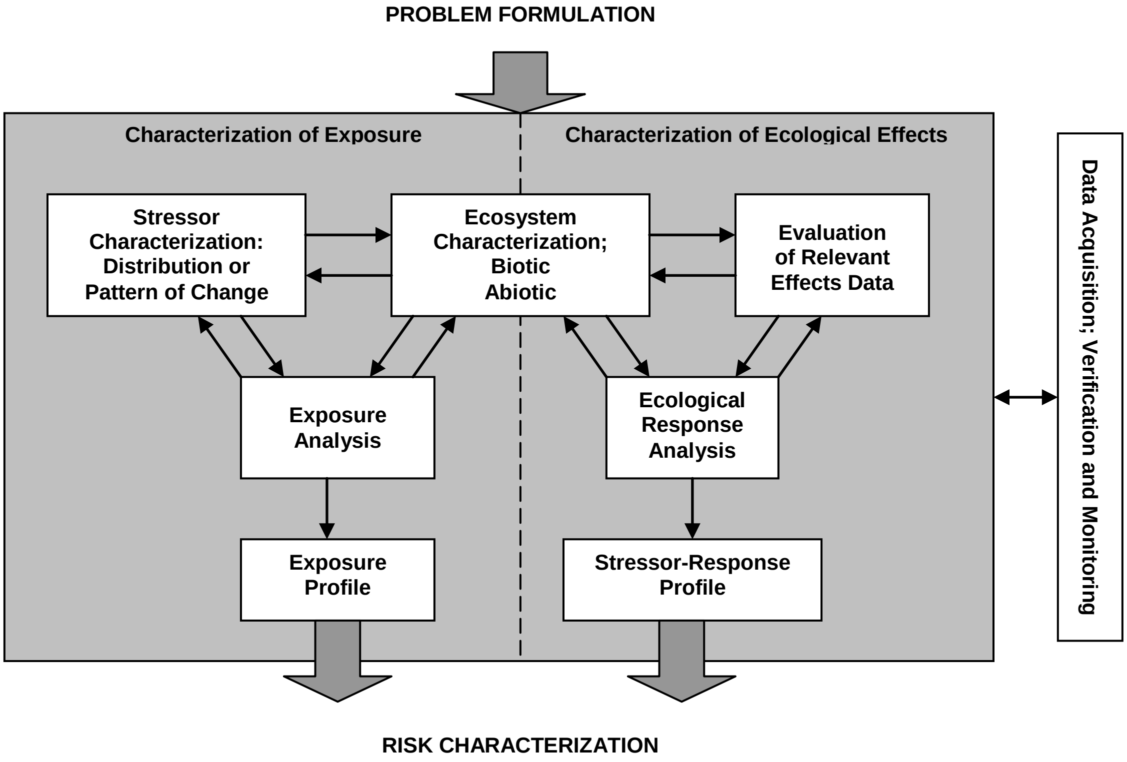


Figure 3.4 - Analytical phase scheme [25]

The *characterization of exposure* stage evaluates the interaction between the stressor and the ecological component. Exposure in this context can be characterized as co-occurrence or contact depending on the relevant stressor and the relevant ecological component. On the basis of exposure scenarios determined during problem formulation phase the exposure profile is developed. Exposure profile quantifies the magnitude and spatial and temporal distribution of the exposure.

Stressors characterization: distribution or pattern of changes determines - as the name suggests - distribution and changes of the stressors in interaction with the environment. To learn more about distribution of chemical stressors a combination of modelling and monitoring data is often used. Monitoring data usually consists of amount of chemical released into the environment and concentration measurement in the influenced media over space and time. For the distribution purpose fate and transport models are usually used; these models are converted from physical-chemical data of relevant chemicals and ecosystem or influenced media properties. The stressors characterization can be also supplied by ground survey, aerial photographs, or satellite imagery. Another important consideration is stressors interaction with the environment. For chemical stressors it is necessary to consider not only primary stressors but also secondary stressors which in this case mean secondary products of environmental fate processes (as degradation, dissociation, etc.).

Ecosystem characterisation analyzes the ecological context of the assessment. Spatial and temporal distribution of the ecosystem components are described as well as the ecosystem attributes which influences the distribution and nature of the stressor. The ecosystem characteristic can greatly modify the ultimate nature and distribution of the stressor. Chemical stressors can be modified by biotransformation due to microbes or by other environmental fate processes such as photolysis, hydrolysis, and sorption. Spatial and temporal distribution of ecological components is also considered in this step. Ecosystem characteristic which influences their exposure to the stressor are also evaluated. This means habitat needs, food preferences, reproductive cycles, and seasonal activities such as migration and selective use of the resources.

Next step is *exposure analysis* which combines the stressors and ecosystem characteristic (spatial and temporal distributions) to evaluate an exposure. The focus of the analysis is dependent on the stressors involved and assessment and measurement endpoints. The most common approach of exposure analysis is to measure concentrations or amounts of stressor and consequently combine them with assumption about co-occurrence, contact, or uptake in the environment. The exposure can be described using models which combine abiotic ecosystem properties, stressors properties, and ecological component characteristic. Selection of the model is done with respect to suitability of particular model for the ecosystem or component of interest, the availability of needed data, and the aim of the assessment. There is the possibility to choose from the range of models - from simple screening-level procedures that require minimum of data to more sophisticated methods that describes the processes more detailed but also need more data.

The information obtained in exposure analysis is used to build an *exposure profile*. The exposure profile quantifies the magnitude and spatial and temporal pattern for the scenarios developed during problem formulation phase. This exposure profile serves then as an input into the risk characterisation phase. To express exposure profile variety of units are usually used. For chemical stressors the dose units (e.g. mg/body weight/day) or concentrations units (e.g. concentration/unit area/time) are usually used. An inherent part of exposure profile is an uncertainty assessment because in many cases the appropriate data are not available or the available data could be of questionable or unknown quality. So the assessors have to deal with many assumptions and the judgement is dependent on their professionalism.

Characterization of ecological effects assesses the interaction between the stressor and the assessment and measurement endpoints. This part of analysis phase begins (as it is shown in the Figure 3.4) with the *evaluation of relevant effects data* which are relevant to the stressor. The analysis then continues by the ecological response analysis; it quantifies the ecological effects caused by the stressor and cause-effect relationship is evaluated. The outcome is *stressor-response profile* which quantifies and summaries the relationship of the stressor to the assessment endpoint.

Evaluation of relevant effects data step evaluates the effects of stressor to the environmental component. The evaluated effect data are strongly dependent on the nature of stressor and the ecological component. The effects can vary from mortality and reproductive impairment in individuals or populations to disruptions of community and ecosystem functions. The evaluation process is a question of professional judgment especially if there is a lack of data. During the data evaluation the attention is paid to their relevance to the assessment and measurement endpoints selected in problem formulation phase. The analyses techniques which will be used are also discussed. The minimization of extrapolation of data is taken into consideration during the appropriate techniques selection. The data choice is also influenced by characteristic of ecosystem potentially at risk. Data from both field observation and laboratory experiments are usually used to evaluate the ecological effects.

Ecological response analysis quantifies stressor-response relationship using data from previous step to evaluate the evidence of causality. Different techniques may be used - statistical methods, mathematical modelling, etc. Firstly stressor-response analysis is conducted. This analysis describes the relationship between magnitude, frequency, or duration of the stressor and the magnitude of the response. The stressor-response analysis is focused on different aspect according to the assessment objectives, the conceptual model, and the type of used data. The relationship between stressor and the assessment endpoint is quantified during stressor-response evaluation step. If the assessment endpoint can be directly measured the analysis is straightforward. If it can not be measured it is necessary firstly established the relationship between stressor and measurement endpoint. Consequently additional extrapolations, analyses, and assumptions are used to predict changes in the assessment endpoint. Measurement endpoints are related to the assessment endpoint according to the logical structure presented in the conceptual model. Professional judgement is an essential part of this evaluation because of lack of standards methods for many of these analyses. In cases of long-term impacts ecological recovery is considered. Ecological recovery is difficult to predict and is dependent on many features - organisms' presence, physical-chemical environmental quality, dispersion, etc. Evaluation of the strength of the casual association between the stressor and the assessment and measurement endpoint is another important aspect of ecological response analysis. This information support and complement the stressor-response assessment. Although the evaluation of casual evidence is not a requirement for the risk assessment it enlarges it.

The results of the characterization of ecological effects are summarized in a *stressor-response profile*. This profile describes stressor-response relationship, extrapolation and additional analysis, and evidence of causality. Ideally it relates magnitude, duration, frequency, and timing of exposure. It is also important to describe the assumptions and uncertainties used during evaluation.

Risk Characterization Phase

Risk characterization is the final phase of the risk assessment; scheme is shown in the Figure 3.5. This phase provides evaluation of the likelihood of adverse effects which occur as a result of exposure to a stressor. Risk characterization phase contains two main steps: *risk evaluation* and *risk description*. The stressor-response profile and exposure profile evaluated in the analytical phase serve as an input. The uncertainties identified during all phases are also summarized and analyzed.

In the *risk estimation* stage the comparison of exposure and stressor-response profiles is conducted as well as estimating and summarizing of associated uncertainties. Generally three different approaches may be used to *integrate the stressor-responses and exposure profiles*: (1) comparing single effect and exposure values, (2) comparing distribution of effects and exposure, and (3) conducting simulation modelling.

The single effect and exposure values approach provides comparison of single effect values with predicted or measured levels of the stressors. The ratio or quotient of the exposure value to the effect value is evaluated; this ratio provides the risk estimation. If the ratio is one or more the adverse effects are likely to occur. This approach is known as Quotient Method and although it is commonly used and accepted it is the least probabilistic of the method described here.

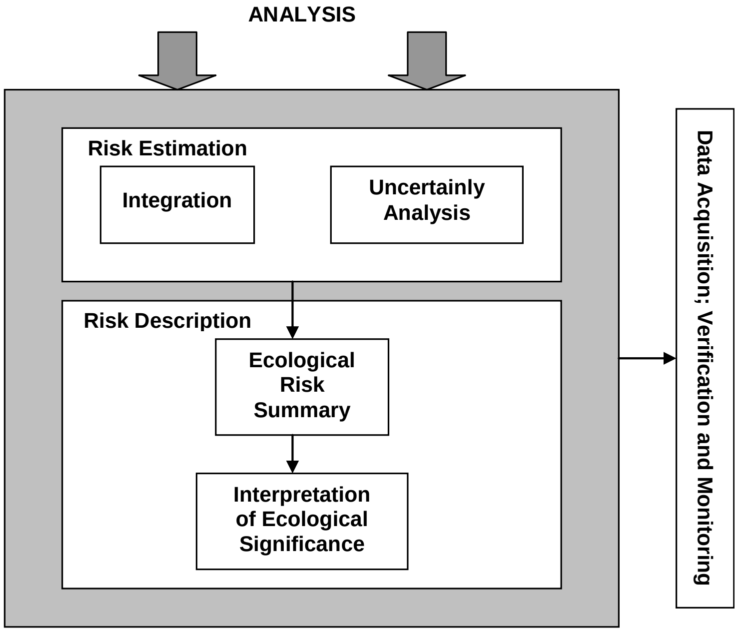


Figure 3.5 - Risk characterization scheme [25]

Second approach - comparing distribution of effect and exposure - uses comparison of distributions of effect and exposure to assess the risks. This makes development of probabilistic risk estimate easier. Risk is then quantified according to the degree of overlap between the two distribution; the more overlap, the greater the risk.

Simulation models which can integrate both stressors-response and exposure profile are used to obtain probabilistic estimate of risk. There are two categories of simulation models: single-species population model and multi-species population model. When selecting the model attention have to be paid to the appropriateness of the model. The single-species model is used to predict direct effect on a single population of concern using measurement endpoints at the individual level. The multi-species model includes aquatic food chain models and terrestrial plant succession models and can be used for both direct and indirect effects.

The *uncertainty analysis* identifies the uncertainty in problem formulation, analysis, and risk characterization phases. From each step of the risk assessment the uncertainty is carried through to be characterized as total uncertainty in this step. The outcome of this analysis is evaluation of total impact of partial uncertainties to the overall risk assessment. If it is possible the ways how to reduce the uncertainty are also described. The major areas of uncertainties are: non complete data, natural variability of stressors and ecological components, and errors in measurement or sampling. In summary, uncertainty analysis provides information how strong or weak the risk analysis is. Uncertainty analysis can also help to make decisions concerning to alternative actions performing as well as which information to obtain to reduce the uncertainty.

Risk description step basically consists of two parts: *ecological risk summary* and *interpretation of ecological significance*. *Ecological risk summary* summaries the results of the risk estimation and the uncertainty analysis and assesses the confidence of the risk assessment by weighting of evidences. The risk estimation is ideally expressed quantitatively; but in many cases only likelihood - qualitative statement - is set. Uncertainties are also summarised qualitatively or quantitatively. Also relative contribution of various uncertainties to the risk assessment can be discussed. Weight of evidence discussion provides insight about confidence of the risk assessment by comparing positive and negative aspects of the used data, including uncertainties. The conclusion of ecological risk summary is usually identification on additional analyses or data that may reduce the uncertainty of the risk assessment.

Interpretation of ecological significance part describes the magnitude of the identified risks to the assessment endpoint. It provides a critical link between the estimation of risks and the communication of assessment results. This step is strongly dependent on professional judgement and can emphasize different aspects depending on the risk assessment. Several aspects of ecological significance that may be considered include nature and magnitude of the effects, the spatial and temporal patterns of the effects, and the potential for recovery when the stressor is removed. These aspects may be used during interpretation phase to place the risks into broader ecological context. This may include discussion of the effects on other ecological components which were not specified in the assessment.

The risk characterization concludes the risk assessment process and provides the basic information for the risk management process. The output of the risk assessment serves as an input for the risk management process.

4. RISK ASSESSMENT TOOL - RISC 4

4.1 Introduction to the Risk Assessment Tools

There exist several tools for the risk assessment according to the purpose of the use. There has been developed number of good methodologies for assessing risk for human health. Methodologies for assessing risk for the environment are not developed so well. An exception present dispersion models for predicting of spreading of contaminants in the atmosphere. There have been developed good tools as software ALOHA or even more well-developed software Effect. Situation concerned to methodologies for surface water, groundwater, or soil risk assessment is not so good. The processes occurring when contaminant enters into these environmental compartments are more complicated thus it needs more sophisticated models. There have been developed models for surface water risk assessment as EUSES and Proteus. For groundwater risk assessment the software RISC 4 can be used.

The software RISC 4 (**R**isk - **I**ntegrated **S**oftware for **C**leanups) was used for evaluating risks at the Grindsted landfill. The RISC 4 is the fourth version of soil and groundwater risk assessment software developed by *BP Oil International (UK)*. It has been developed in order to eliminate the potential for adverse human health impacts (both carcinogenic and non-carcinogenic risk) and to evaluate ecological risk. The ecological risks assessment provide fate and transport modeling of contaminant spreading in vadose zone, saturated zone, and volatilization from soil into air. Then the receptor point concentrations are estimated. The main applications of this software are estimation of human health risk from exposure to contaminated media, estimation of risk-based clean-up levels in various media, performance of simple fate and transport modeling, and evaluation of potential ecological impacts to groundwater, surface water end sediment.

4.2 Risk Assessment by the RISC 4 Tool

Risk assessment conducting by the software RISC 4 is run in six steps. There are different steps for human health risk assessment and for ecological risk assessment. In the following text the attention is focused on ecological risk assessment modeling. The Figure 4.1 shows the six steps of ecological risk assessment. However the first step - *chemicals of concern selection* - is the same for both of them. The procedure starts differ from step two where the human health risk assessment or ecological risk assessment are chosen.

○ Human Health
● Ecological/Water Quality

Figure 4.1 - Step 1 to step 6 of ecological risk assessment in program RISC 4 [51]

Next captures describe each step of the environmental risk assessment in details.

4.2.1 Step 1 - Chemicals of Concern Selection

The software includes chemicals database with 86 chemicals. The chemicals of concern are chosen from this database or, if they are not included, it is also possible to add new chemicals. The database provides information about the chemicals as name, it’s synonyms, CAS number and naturally physical-chemical properties - molecular weight, density, vapor pressure, solubility, partitioning coefficients K_{ow}, K_{oc}, K_d, Henry's low constant, degradation, diffusion in air and water. Toxicity parameters of the chemicals are also included in the database. It is also possible to change the chemical-physical properties and toxicity parameters of chemicals already included in the database.

4.2.2 Step 2 - Determination of Exposure Pathways

As mentioned above in the step two the human health risk assessment or the environmental risk assessment has to be chosen. According to this setting the other steps differ between the human health risk assessment and the ecological risk assessment. Even if some settings are quite similar the final assessment is of course different.

When the ecological risk assessment is chosen then only surface water modeling or surface water mixing with groundwater has to be chosen. For the mixing model the fate and transport model has to be defined. There are three models available for estimation of groundwater concentration downgradient: vadose zone model, saturated zone model, and dissolved source model. Also model for estimation of the surface water pollution concentration (caused by groundwater percolation) is available; it is groundwater mixing with surface water. Evaluation mechanisms of these models are described bellow.

Vadose Zone Model

The vadose zone model assumes the source zone to be located in the vadose zone. The model then simulates contaminant transport from the source through unsaturated soil. The purpose of vadose zone model is to predict leaching from soil to groundwater and volatilization losses. In the Figure 4.2 you can see the process simulated by the vadose zone model.

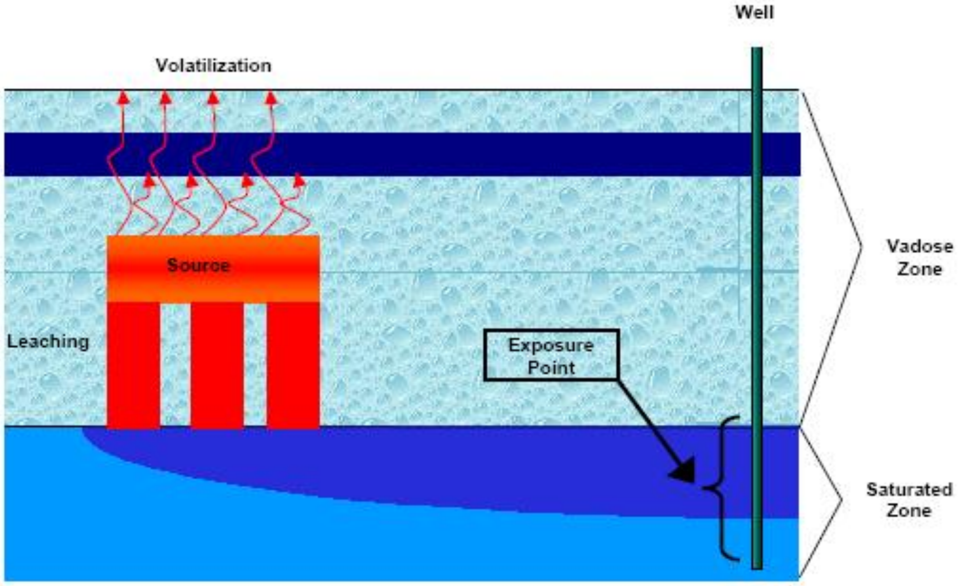


Figure 4.2 - Scheme of the vadose zone model [51]

In this paragraph the main applications and limitations of the vadose zone model are described. The model evaluates the mass leaching to groundwater from the source in the vadose zone. It considers source depletion due to leaching and volatilization loses. It can not simulate the movement of NAPL because it is only dissolved phase model. However it accounts for the presence of NAPL by limiting the dissolved phase concentration in the source area to the chemicals' effective solubility limit; otherwise the concentrations could be strongly over-estimated. Degradation is considered in the dissolved phase for the area between source and groundwater table. The vadose zone model is automatically linked with dissolved source model (described below) so it allows calculation of groundwater concentrations. The model assumes that the vadose zone and the aquifer below the source are "clean" at the beginning of the simulation. The size of the source in the vadose zone is mapped onto the groundwater table and becomes a footprint for the groundwater source size.

For the purpose of modeling the fate and transport processes the source is assumed to be well-mixed finite source which depletes with time, the vadose zone above the source is assumed to be one-dimensional and at a pseudo-steady state. Solute transport occurs beneath the source via advection and dispersion, and because of a first-order reaction a mass loss may occur. For transport calculation the one-dimensional transport equation (including adsorption) is used.

$$R\frac{\partial C_w}{\partial t} = D_x \frac{\partial^2 C_w}{\partial x^2} - v\frac{\partial C_w}{\partial x} - \mu C_w$$

Equation 4.1

where:		
	C_w	dissolved phase concentration of chemical [mg/L]
	D_x	dispersion coefficient in the unsaturated zone [cm^2/d]
	v	seepage velocity [cm/d]
	μ	first-order decay coefficient for chemical [1/d]
	x	distance below the source (measured positively downward) [cm]
	t	time [d]
	R	retardation factor [-]

The leachate concentration C_w leaving the source is assumed to decay exponentially with time.

For the leachating and percolation rate evaluation a unit gradient approach is used. The unit gradient approach assumes that the pressure head in the soil profile is constant as well as moisture content. This is the main simplification of the real process. However the aim of concentration modeling is to estimate average condition for long period (for purpose of the risk assessment from 7 to 30 years). So for this objective the unit gradient approach is working reasonably well. Briefly, Darcy's law equation is used for the unit gradient approach.

$$q = k_r \cdot K_{su}$$

Equation 4.2

where:		
	q	infiltration rate or net recharge rate [cm/d]
	k_r	relative permeability [-]
	K_{su}	hydraulic conductivity of the unsaturated zone (if it were fully saturated) [cm/d]

When using the RISC 4 user is asked to input infiltration rate q and hydraulic conductivity K_{su} the Darcy's equation is used to calculate relative permeability k_r.

Dissolved Source Model

The dissolved source model simulates dissolved phase contaminant transport in the groundwater aquifer. This model can be used to predict contaminant concentration in groundwater at a receptor well or as a source of volatile compounds emissions into buildings. This model is also useful if soil data are missing or if the contamination is already spread in the groundwater so it is not necessary to model the leachating process. The Figure 4.3 shows a scheme of the dissolved phase model and a process simulated by the model.

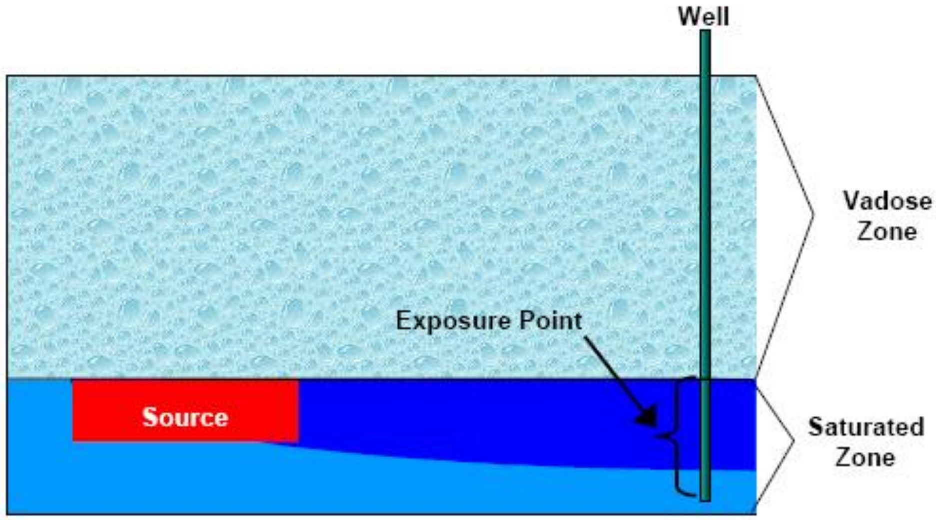


Figure 4.3 - Scheme of Dissolved phase model [51]

The model accounts for following fate and transport models: one-dimensional flow, three-dimensional dispersion, retardation (adsorption), and degradation. For the uniform flow the three-dimensional dispersion equation is used.

$$R\frac{\partial C_w}{\partial t} = D_x\frac{\partial^2 C_w}{\partial x^2} + D_y\frac{\partial^2 C_w}{\partial y^2} + D_z\frac{\partial^2 C_w}{\partial z^2} - v\frac{\partial C_w}{\partial x} - \mu C_w + \frac{M}{\theta} \qquad \textbf{Equation 4.3}$$

where:

C_w	concentration of component in the aqueous phase[g/L]
x	distance in the direction of groundwater flow [m]
y	cross-gradient distance (from centreline of plume) [m]
z	vertical distance positive downwards from water table [m]
D_x	dispersion coefficient in the direction of groundwater flow [m^2/d]
D_y	transverse dispersion coefficient [m^2/d]
D_z	vertical dispersion coefficient [m^2/d]
v	seepage velocity [m/d]
μ	first-order decay coefficient for chemical [1/d]
t	time [d]
R	retardation factor [-]
M	source term (mass flux) for chemical [g/d/m^3]
θ	effective porosity of the saturated zone [cm^3/cm^3]

The aquifer is considered to be infinite in depth and width. The source is assumed to be of a constant concentration specified for certain duration (pulse) or it may vary with time. The contaminant mass is assumed to be instantly dissolved and mixed uniformly over the source.

Saturated Zone Model

This model simulates transport of dissolved chemicals from a soil source zone or near the water table. The position of the source relative to the water table is important because there are two different processes - rainwater infiltration and groundwater flow through the source - contributing to the contamination of the aquifer. The positioning of the source relative to the water table may vary during year because of the water level fluctuation. In this model the source concentration is defined as a total source concentration. This soil concentration may be above the residual limit.

The application of this model is the same as for dissolved source model; it can be used for predicting of contaminant concentration in groundwater at a receptor well or as a source of volatile compounds emissions into buildings. Scheme of the model is shown in the following figure.

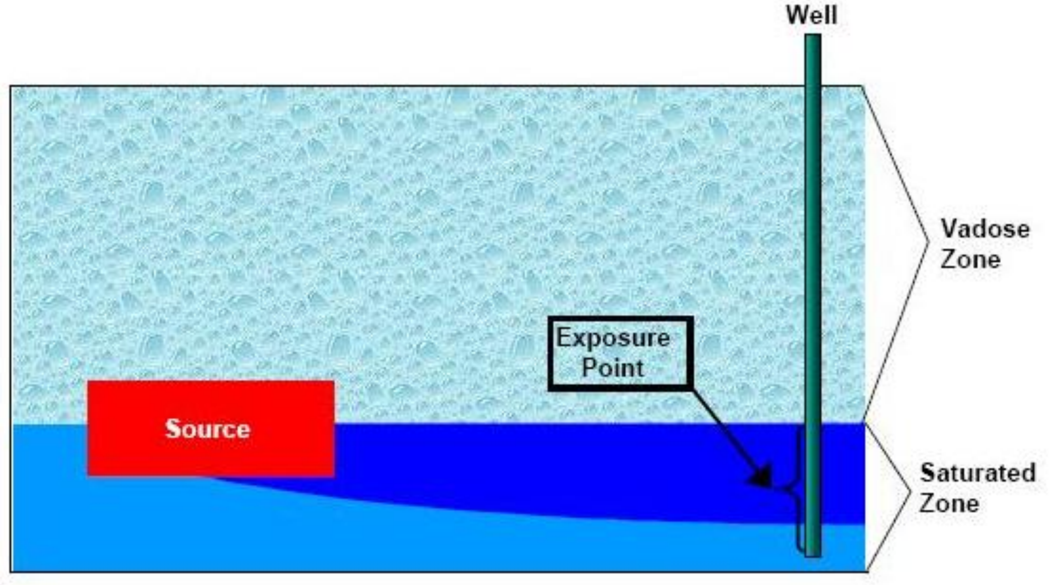


Figure 4.4 - Scheme of the saturated zone model [51]

This model basically consists of source zone leaching model and dissolved source transport model (this is identical to the dissolved source model described above). The source model is used for estimating the mass loading rate (which is used as an input into dissolved phase model) based on the concentration of chemicals in the soil.

The mass of chemicals in the source above the groundwater table is supposed to leach due to infiltration, while the mass of chemicals in the source below the water table is assumed to leach horizontally with the groundwater flow. The leachte rates are calculated from effective solubility or from equilibrium partitioning. The equilibrium dissolved phase concentration is estimated and is supposed to be constant untill the source is depleted.

The source is defined by specifying of a total soil concentration for each modeled chemical and the total volume of the source. The total initial mass of contaminants in the source is calculated according to the following equation.

$$Mass = \frac{C_T \cdot \rho_b \cdot H \cdot W \cdot L \cdot \left(E6cm^3/m^3\right)}{\left(000\ g/kg\right)}$$ **Equation 4.4**

where: *Mass* total initial mass in saturated source [mg]
C_T total concentration in source [mg/kg]
ρ_b soil bulk density [g/cm^3]
H height of source [m]
W width of source [m]
L length of source [m]

The total initial mass is depleted when the dissolved contaminant is carried with groundwater flow. The depletion (and hence the contamination source for dissolved model) is calculated by estimating the dissolved phase contaminant concentration in the source volume and it is assumed that this concentration leaves the source with groundwater flow. If hydrocarbons residual phase is presented the dissolved phase source concentration for each chemical is assumed to be equal to its effective solubility.

This model also accounts only for transport of dissolved phase contaminants; it does not simulate the movement of NAPLs. The aquifer is considered to be homogenous and uniform. The water table fluctuation is assumed to have no influence on the groundwater flow.

Surface Water Mixing and Sediment Partitioning Model

This model is used when mixing of groundwater with surface water occur. It estimates concentration of contaminants in surface water and sediment assuming that contaminated groundwater is percolating into the surface water. Concentration of contaminants in groundwater adjacent to the surface water may be directly entered in the model or one of the fate and transport models may be used to calculate the concentrations.

There are two types of surface bodies which could be modeled: (1) lakes, estuaries or large water bodies and (2) rivers, creeks or streams. Sediment model is simple partitioning model which predicts the contaminant concentration that is sorbed to the sediment in the area of groundwater contaminant plume passing through the sediment to the surface water. In the sediment model no degradation is accounted for.

The main applications of surface water mixing model are: (1) to estimate potential impact of adjacent contaminated groundwater to surface water body, (2) to determine an impact of contaminated groundwater to surface water when the source of contamination is farer from the surface water the model can be linked with groundwater fate and transport model, and (3) to evaluate potential length of surface water body shore which is impacted by groundwater. In the Figure 4.5 is shown the surface water mixing model geometry from an areal perspective.

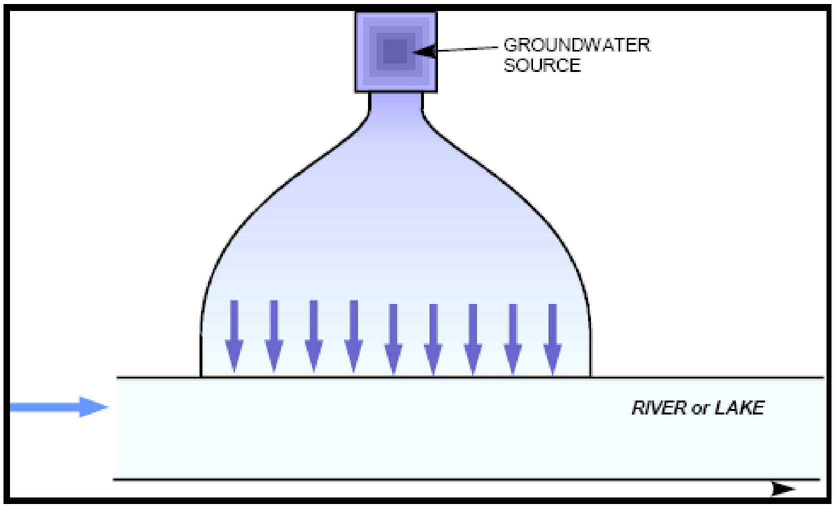


Figure 4.5 - Surface water mixing model geometry [51]

The model is based on simple well- mixed model where the concentration through the surface water body is equal throughout. This approach is used in the RISC 4 for both rivers and lakes. Advection and dispersion is not account for in the well-mixed model.

The calculations of the well-mixed model are based on the principle of mass balance:

$$V\frac{dC_{sw}}{dx} = W(t) - QC_{sw} - \mu_{sw} V C_{sw} \qquad \textbf{Equation 4.5}$$

where:	$W(t)$	mass loading [mg/d]
	V	volume of surface water for mixing [m^3]
	C_{sw}	concentration of contaminant in surface water [mg/m^3]
	t	time [d]
	Q	inflow/outflow rate [m^3/d]
	μ_{sw}	decay rate of chemical in surface water [d^{-1}]
	x	distance downgradient in the river; parallel to the surface water body edge for the lake [m]

The groundwater is assumed to intersect the river in the right angle or perpendicular to the lake edge.

The sediment concentrations are calculated using the equilibrium partitioning equation:

$$C_{sed} = C_{gw} \cdot K_d$$

Equation 4.6

where:	C_{sed}	concentration in sediment [mg/kg]
	C_{gw}	concentration in groundwater in centerline of plume (estimated by RISC 4 model or user specified) [mg/L]
	K_d	soil-water partitioning coefficient [ml/g]

For inorganic chemicals the K_d value is directly entered in the RISC 4 chemical database but for organic chemicals it is calculated on the basis of fraction of organic carbon (f_{oc}) and chemical specific organic-carbon partitioning coefficient (K_{oc}).

$$K_d = f_{oc} \cdot K_{oc}$$

Equation 4.7

The model also calculates the groundwater inflow rate. It is calculated using Darcy's low equation:

$$Q_{gw} = K_{sw} \cdot d_{sw} \cdot L_{reach} \left(\frac{h_{gw} - h_{sw}}{L_f} \right)$$

Equation 4.8

where:	Q_{gw}	groundwater inflow rate [m^3/d]
	K_{sw}	hydraulic conductivity of the groundwater-surface water interface (also the hydraulic conductivity of the aquifer may be used) [m/d]
	d_{sw}	thickness of groundwater that ends up discharging in the surface water body [m]
	L_{reach}	length of surface water body shore impacted by groundwater [m]
	L_f	distance along flow line between h_{sw} and h_{gw} [m]
	h_{sw}	river/lake water level [m]
	h_{gw}	groundwater hydraulic head [m]

The hydraulic gradient between surface water and groundwater may differ from overall hydraulic gradient of the aquifer away from the surface water body edge. The Figure 4.6 shows cross-sectional schema with the variables.

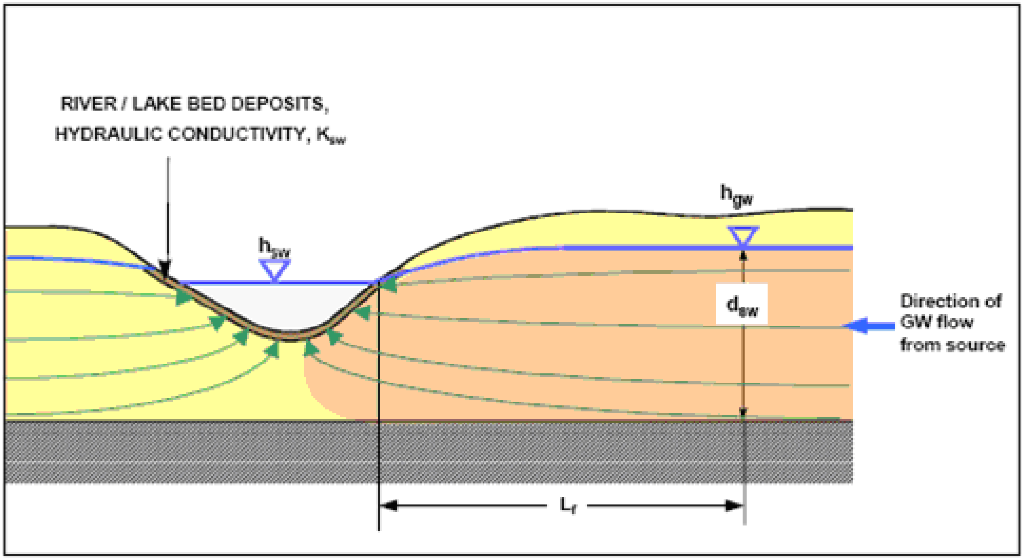


Figure 4.6 - Cross-sectional model geometry [51]

The length of reach (length of surface water body shore impacted by groundwater, L_{reach}) can be either entered by user or calculated by RISC 4 if the linked model is used. If the linked model is used the length of reach, L_{reach}, is a function of the plume width where it intersect the surface water body. An assumption made is that the concentration across the plume width is constant. The width of impact is calculated to the point of 5 (10) % of centerline concentration when the plume is in steady state. The Figure 4.7 gives an areal schema how the length of reach is calculated.

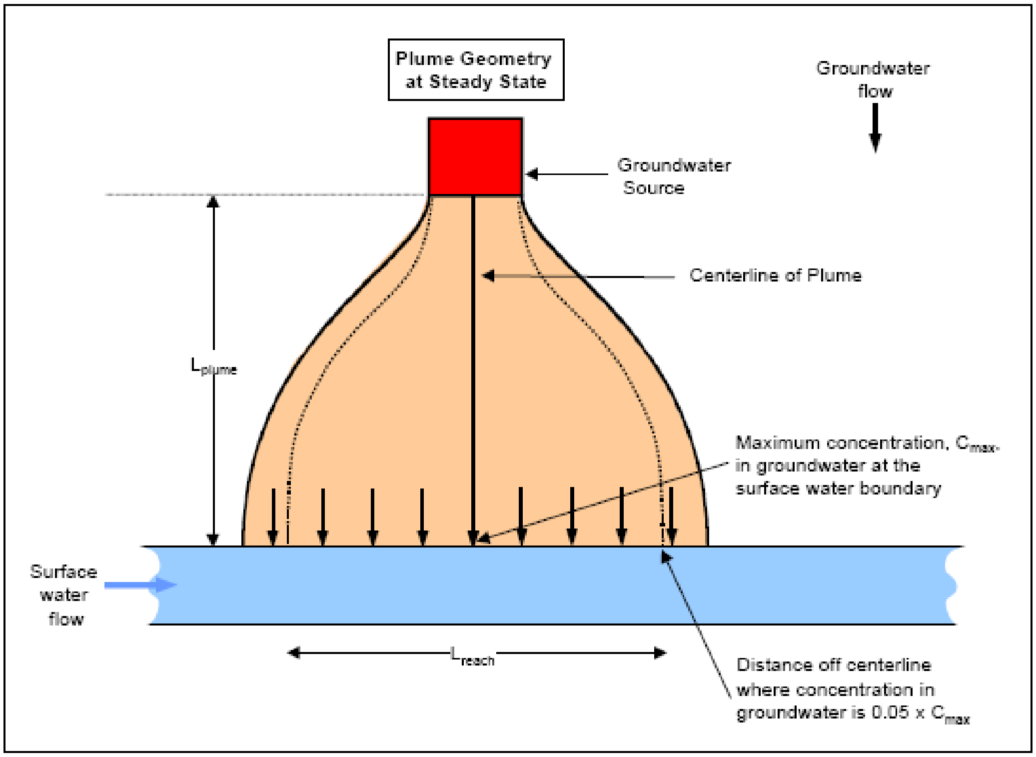


Figure 4.7 - Schema of calculating the length of reach, L_{reach} [51]

The calculation of the length of reach assumes that the groundwater source is continuous and steady-state for the length of the simulation time. It is therefore calculated the worst case width of the plume at the surface water body edge. This conservative value is then used in the calculation of groundwater loading to the surface water.

$$Q_{gw} = K_{sw} \cdot d_{sw} \cdot L_{reach} \left(\frac{h_{gw} - h_{sw}}{L_f} \right) \qquad \textbf{Equation 4.9}$$

where:

Q_{gw}	groundwater inflow rate [m^3/d]
K_{sw}	hydraulic conductivity of the groundwater-surface water interface (also the hydraulic conductivity of the aquifer may be used) [m/d]
d_{sw}	thickness of groundwater that ends up discharging in the surface water body [m]
L_{reach}	length of surface water body shore impacted by groundwater [m]
L_f	distance along flow line between h_{sw} and h_{gw} [m]
h_{sw}	river/lake water level [m]
h_{gw}	groundwater hydraulic head [m]

4.2.3 Step 3 - Determination of Receptor Point Concentration

The third step is divided into four substeps: *3a - description of the site properties*, *3b - entering of source concentration, 3c - running of fate and transport model*, and *3d - viewing the results*.

Step 3a - Description of the Site Properties

The step 3a asks user for detailed specification of the environmental component involved; specification of unsaturated zone, aquifer, surface water body (river or lake), and specification of source geometry too (this specification differ a bit according to model selected in the step two).

Information about unsaturated zone needed are: infiltration rate, thickness of vadose zone, total porosity, residual water content, saturation conductivity of the vadose zone, fraction of organic carbon, soil bulk density. Aquifer characteristics are following: hydraulic gradient, effective porosity, fraction of organic carbon, hydraulic conductivity, soil bulk density, dispersivity (longitudinal, transversal, vertical). Surface water body is specified as following: distance of groundwater source to surface water edge, surface water flow rate, cross-sectional area (valid only for river), volume of lake (if lake is selected), hydraulic gradient between surface water and groundwater, thickness of aquifer entering the surface water body, hydraulic conductivity of surface water bed, fraction of organic carbon in sediment. Source geometry characteristics are: thickness, length, and width of contamination, and may be depth to the top of contamination (according to the model selected in step two).

Step 3b - Entering of Source Concentration

In this step the found concentrations of chemicals of concern are defined. There are two possibilities how to enter them - single value or sample data base. Sample data base is used when more than one measured concentration exists for the chemicals of concern. The data may consist of samples from different locations of the site or from multiple samples taken at one location over time.

Step 3c - Running of Fate and Transport Model

Here only the simulation time is set and the model is run for each chemical of concern.

Step 3d - Viewing the Results

The step 3d shows results calculated by the model selected in the step two as tables or graphs. Model input summary and chemical-specific output file are displayed as tables and calculated concentrations are displayed as tables and graphs.

4.2.4 Step 4 - Surface Water and Sediment Criteria

In the step four the calculated results are compared with regulatory standards from different countries. The program includes databases with the regulatory standards so the user can chose which standard he wants to compare with his results. These standards values are attached to the program as Supplemental Spreadsheet Tool - Water Quality.

Two types of criteria are used: water quality criteria and sediment criteria. The surface water results may be compared with five types of criteria: Australia and New Zealand Water Quality Guidelines firstly published by ANZECC (Australian and New Zealand Environment and Conservation Council), US AWQC (United States Ambient Water Quality Criteria) published by U.S. EPA, United Kingdom Environmental Quality Standards (UK EQS), European Commission Water Quality Objectives (EC WQO), Canadian Council of Ministers for the Environment Fresh Aquatic Life Guideline (CCREM). The sediment criteria that may be used are: NOAA (National Oceanic and Atmospheric Administration - U.S.) - PEL (probable effect level) and NOAA - UET (upper effects threshold) [51].

4.2.5 Step 5 - Calculating of Clean-up Levels

This step provides the clean-up levels calculation (sometimes also called back-calculation). The user must specify the target concentrations and the software calculate the “allowable” source concentration (clean-up levels). The clean-up levels represent source and/or receptor point concentrations for the chemical of concern which can not be exceeded for the outlined scenario.

4.2.6 Step 7 - Viewing of Results

The step seven shows the clean-up calculation results. It shows site specific target levels and original source concentrations of chemicals of concern. If no data about site specific target concentration are defined chemical solubility is used as the target level.

The captures above do not provide overall overview of the software RISC 4 features. There are more applications concerned to human health risk assessment but they are not discussed in the text because human health risk assessment is not the objective of this study. The RISC 4 description has been focused to the ecological risk assessment and conducting of the ecological risk assessment via the RISC 4 program.

4.3 Input Data Requirements

Input data requirements for the RISC 4 modeling are summarized in the Table 4.1.

Table 4.1Summary of RISC 4 data requirement

chemicals	source		unsaturated zone	aquifer	surface water recipients	
	dissolved model	vadose model			lake	river
CAS Number	thickness	thickness	infiltration rate	hydraulic gradient	distance to SW edge	distance to SW edge
molecular weight	length (in the direction of GW* flow)	length (in the direction of GW* flow)	thickness of vadose zone	effective porosity	hydraulic conductivity of SW* bed	hydraulic conductivity of SW* bed
vapor pressure	width (perpendicular to GW* flow)	width (perpendicular to GW* flow)	total porosity	fraction of organic carbon	thickness of aquifer entering SW*	thickness of aquifer entering SW*
solubility	concentration of chemicals in the source	concentration of chemicals in the source	residual water content	hydraulic conductivity	hydraulic gradient between GW* and SW*	hydraulic gradient between GW* and SW*
Henry's low constant		depth to top of contamination	saturated conductivity	soil bulk density	surface water flow rate	surface water flow rate
log K_{ow}			value of Van Genuchtens	longitudinal dispersivity	volume of lake	cross-sectional area
K_{oc}			fraction of organic carbon	transversal dispersivity	fraction of lake volume for mixing	fraction of cross-sectional area for mixing
degradation (high/end)			soil bulk density	vertical dispersivity	fraction of organic carbon in sediment	fraction of organic carbon in sediment
degradation (low/end)						

*GW - groundwater

*SW - surface water

5. GRINDSTED LANDFILL

5.1 Basic Information

Grindsted landfill is situated in western part of Denmark respective in Jutland close to a town Grindsted (see the Figure 5.1). The landscape is flat with heath and small woods.

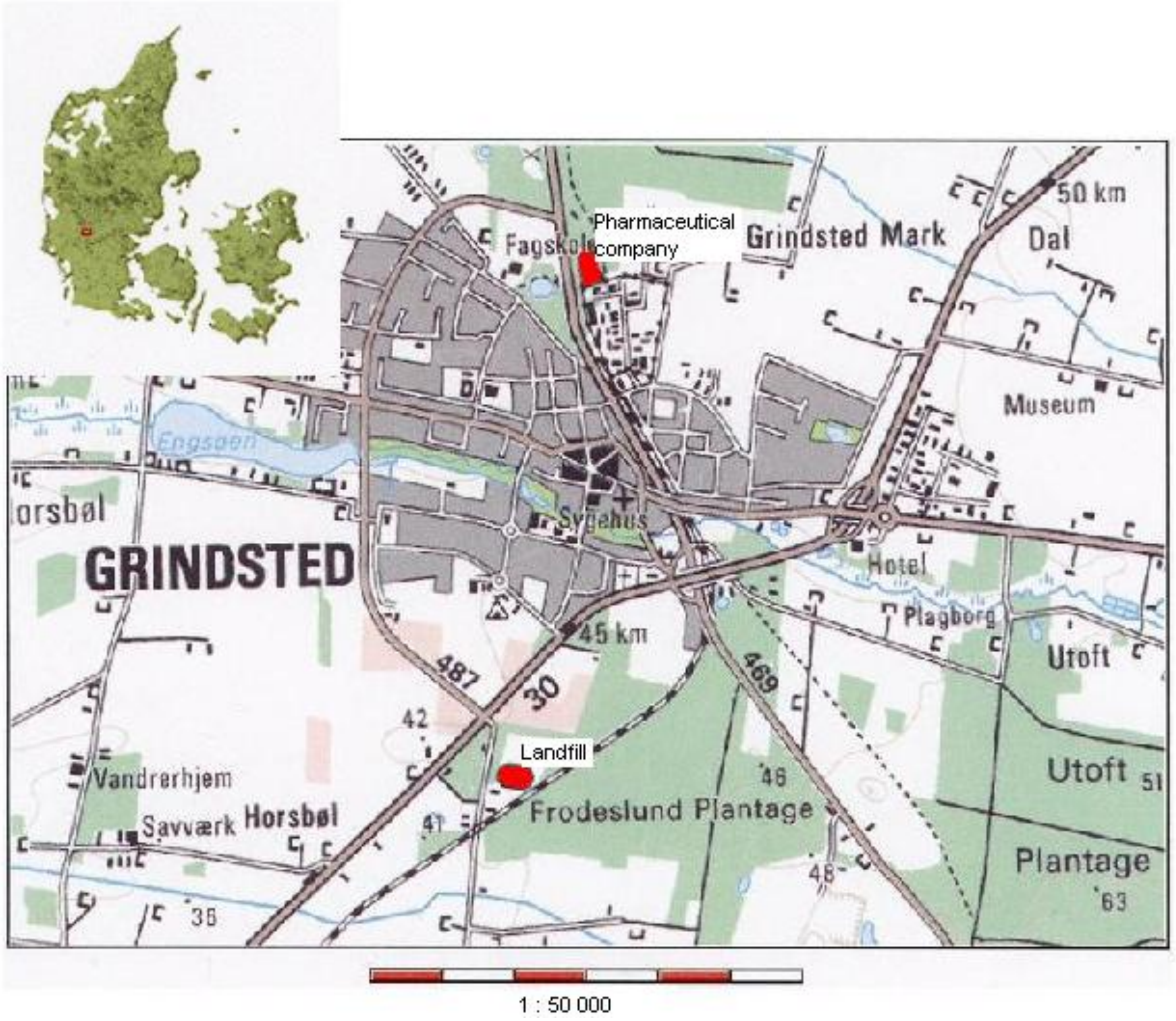


Figure 5.1 - Location of the Grindsted landfill and the pharmaceutical company

Leachate from the landfill contaminates groundwater bellow the landfill, contaminants are subsequently spread in the direction of groundwater flow, and they may also cause contamination of surface water recipients - river and lake because they are located in the direction of groundwater flow (north-west direction). The most threatening pollution comes from the industrial waste. The pharmaceutical company which has been disposing its waste to the landfill is situated in the north-east part of the town Grindsted (see the Figure 5.1); north from the landfill. The soil beneath the pharmaceutical company is also contaminated by several chemicals due to spills during production. The amount of contamination is unknown. Flow direction of groundwater beneath the company is south-west (it means in direction of the river and the lake). This contamination may also contribute to the contamination of the river and the lake. But this contamination is not considered in this study. The target of this study is to assess risks for groundwater and surface water recipients (the river and the lake) which pose the Grindsted landfill.

5.2 Landfill History

The landfill has been created in 1930 on top of the original ground surface. No liners and leachate collection systems were built. Officialy it was closed in 1977; but significant amount of waste was disposed here after the official closure. The main part of waste was landfilled in the 1960's and 1970's. Total amount of waste placed here is around 300 000 tons (500 000 m^3) [43]. It was used for several kinds of disposal - it includes mixture of waste types, liquids, and viscous industrial waste. The whole landfill area at the end of the use in 1977 was 10 ha. The landfill is maximum 8 m high with an average 5 m [11]. The leachate from the landfill respective from upper part of aquifer has been characterized as dilute methanogenic phase leachate.

In 1973 has been carried out an investigation of waste composition. Percentage amount of waste composition has been estimated: municipal solid waste represents 20% of whole amount; bulky waste, garden and street waste 5%; industrial waste 20%; sewage treatment sludge (with 80% water content) 30%; and demolition waste 25% [38].

Until 1973 was the waste disposal rather uncontrolled. From 1973 was the waste compacted and covered with a sandy soil layer every day. The liquid and viscous waste has been placed to lagoons dug into soil or waste. To prevent spreading of liquid waste the lagoons were surrounded by earth embankments. The lagoons have been located in the mid-northern and north-easten patrts of the landfill. A small lagoon has been also placed at north-western border [38].

Significant amount of waste was placed here after the official closure in 1977. Between 1980 and 1983 the disposal still had taken place, but only solid waste was disposed here from 1980. After 1983 no waste was placed at the landfill.

The final soil cover is extremely uneven. The thickness varies from 10 to 30 cm on the western and eastern part of the slope and from 50 to 150 cm on the rest of the landfill. Calculations show that from 1983 till 1990 the waste had settled - in average 1m [37].

The industrial waste comes from a pharmaceutical company producing sulphur containing sulpho-drugs, vitamins, and similar products. The company has been landfilling here its waste from 1962 to 1975. The industrial waste consists of liquids and solid waste. The amount of the chemical waste has been estimated to 85 000 tonnes. The main part of the pharmaceutical waste has been activated carbon and filter aid used in purification of sulfonamides, barbiturates, and water-soluble vitamins. Also calcium sulfate and sodium chloride, pharmaceutical compounds, and distillation residues have been disposed at the landfill [35]. The pharmaceutical company has been using also aromatic hydrocarbons as extraction agents or as active compounds in the reactions. Benzene, toluene, and xylenes have been used in the production. The hydrocarbons used here were "technical grade" which means that other hydrocarbon by-products have been presented as well [38].

5.3 Wells Installation

Surveys on the landfill started at the end of the eighties of the last century. It has been done by Technical University of Denmark, Institute of Environment & Resources. The survey has been focused on the history of the waste disposal at the landfill, area variation of leachate composition, hydrogeology of the site, and leachate migration patterns in the groundwater along the borders of the landfill. Also aerial photographs of the landfill have been taken during this survey. The aerial photographs are shown in the Appendix A.

In order to this survey there were installed different types of wells - piezometers, profile, and leachate wells. The piezometers serve for studying of groundwater flow direction, the profile wells for investigations of groundwater quality as a function of depth and the leachate wells for investigations of leachate composition. The location of the wells is shown in Figure 5.2.

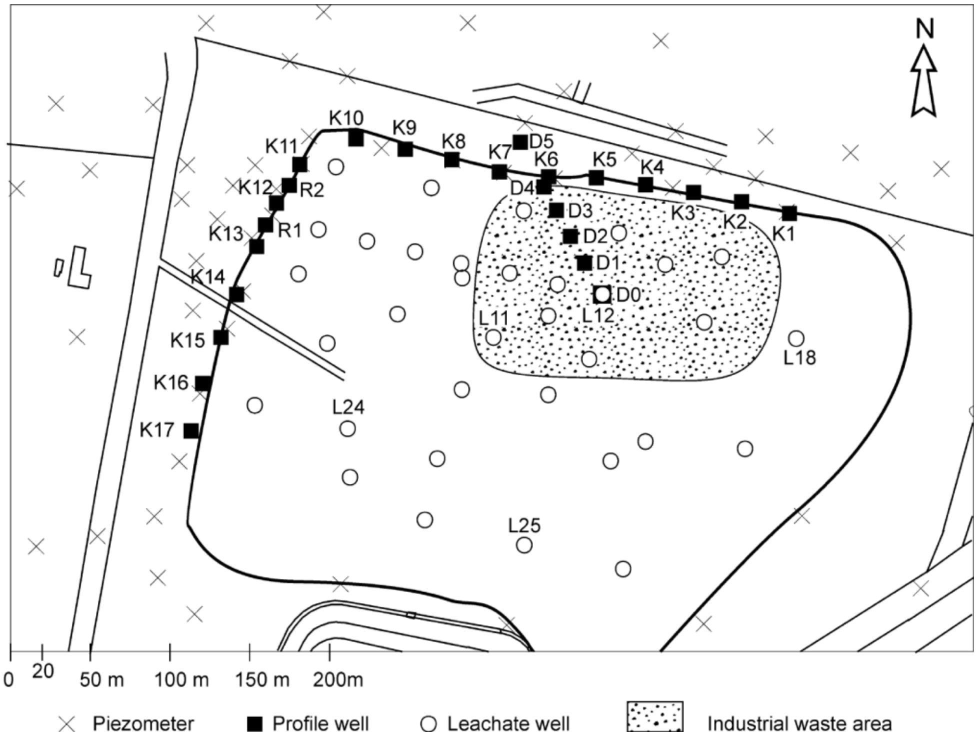


Figure 5.2 - Location of piezometers, profile, and leachate wells; Location of industrial waste area/hot spot [37]

Piezometers have been made from polyvinyl chloride (PVC) tube; the diameter is 25 mm and at the bottom is 40 cm long screen. These wells are installed from 2 to 3 meters below the surface. In total 150 piezometers have been installed in the area surrounding the landfill; it covers area around 3 km^2 [37].

The majority of the profile wells have been installed along the landfill borders in the north-west part of the landfill - it means in the direction of groundwater flow. These wells are constructed from ¾ inch (2 cm) iron pipes rammed into the ground by pneumatic hammer. The pipes are equipped with 10 cm long iron screen and Teflon check valves [37].

There have been installed 31 of leachate wells. The wells are constructed from ¾ inch (2 cm) iron pipes (as well as profile wells) rammed by pneumatic hammer through waste layer into the underlying aquifer. The iron pipes are fitted with tips supplied with 10 cm long iron screens. The bottom of the screen was placed 35 cm under the groundwater table [37].

The wells are still presented at the landfill. During the current survey it was supposed to use the leachate wells to take groundwater samples.

5.4 Geology and Hydrogeology

Grindsted landfill is located on a glacial outwash plain. Aquifer beneath the landfill is around 68 m thick and consist of two upper sandy layers (glaciofluvial sand and micaceous sand), a thin clay/silt layer, and a lower sand layer (miocene sand).The aquifer is at the bottom bounded by miocene clay layer but its depth is unknown [3]. Schematic cross-section area of the aquifer is shown in the Figure 5.3.

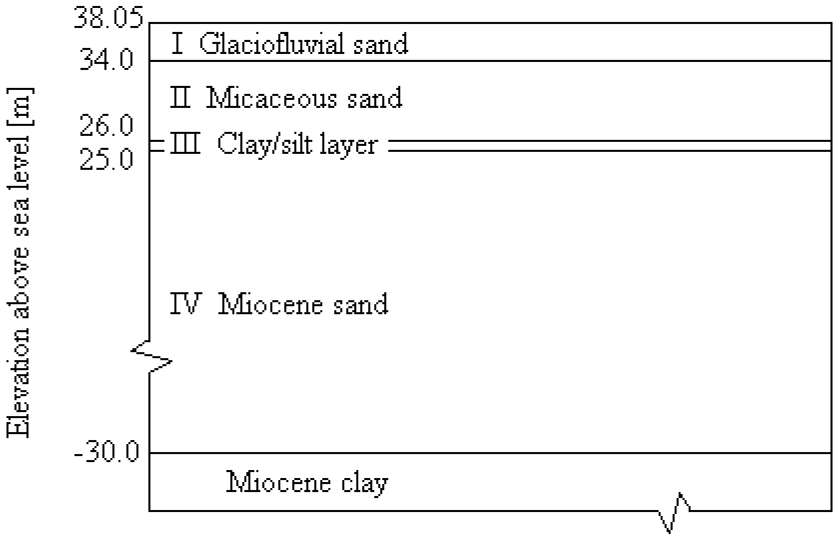


Figure 5.3 - Scheme of cross-section area beneath the landfill

Upper aquifer with glaciofluvial and micaceous sandy layers is approximately 10 to 12 m deep. The upper layer - glaciofluvial sand (from quaternary period) is 5 to 7 m thick. Underlying micaceous sand layer is from 4 to 6 m thick [11]. These two layers are locally separated by discontinuous silt and clay layers [10]. The clay/silt layer is not well defined; according to borehole samples the thickness of the layer has been estimated to 1 m at an approximate depth 12 m. The clay/silt layer extends over a large area of the landfill [10]. The lower aquifer (miocene sandy layer) has been studied only a little. Its thickness has been estimated to 55 m [3].

Hydraulic conductivities have been measured only for two upper sandy layers. The average measured hydraulic conductivity of glaciofluvial sandy layer is $4.6 \cdot 10^{-4}\,m \cdot s^{-1}$; values varied from $9.7 \cdot 10^{-5}\ m \cdot s^{-1}$ to $1.3 \cdot 10^{-3}\ m \cdot s^{-1}$. While micaceous sandy layer average measured hydraulic conductivity is $0.9 \cdot 10^{-4}\,m \cdot s^{-1}$; values varied from $1.8 \cdot 10^{-5}\,m \cdot s^{-1}$ to $2.0 \cdot 10^{-4}\,m \cdot s^{-1}$ [3]. The variance of the log-normalized hydraulic conductivities is 0.47 for the glaciofluvial layer and 0.41 for the micaceous layer. The small variance of the hydraulic conductivity of the both layers indicates a homogenous aquifer [11].

The overall groundwater flow direction is northwesterly with the hydraulic gradient of 0.0012 [34]. But significant seasonal variations in groundwater flow directions have been observed. Figure 5.4 shows streamlines of different locations of the landfill area which are drown on the basis of isopotential curves.

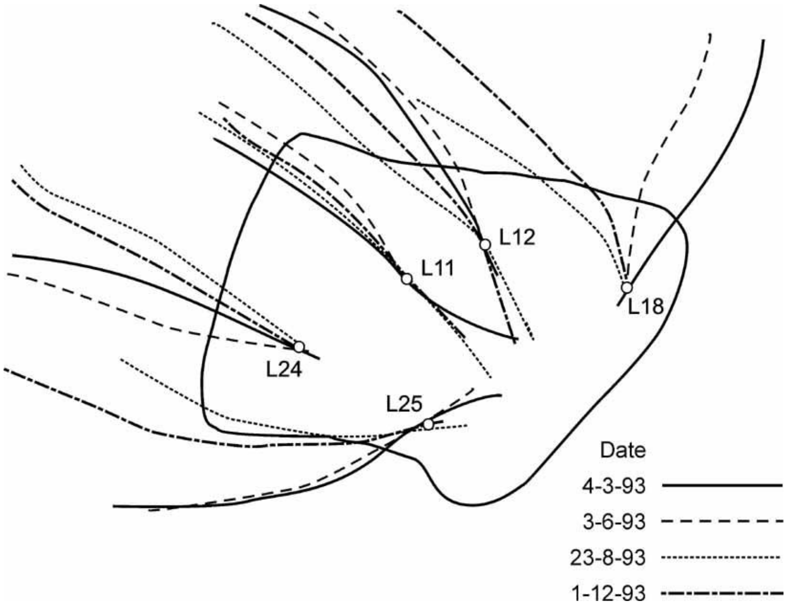


Figure 5.4- Streamlines at different location of the landfill [37]

Especially in north-eastern part of the landfill respective in well L18 the seasonal variation are really significant. There is 90° angle between streamlines from March 1993 to August 1993. In the southern part (wells L25 and L24) the variations are also large while in the middle part of the landfill (L11) there are almost no variations or very minor variations of groundwater flow [37]. This variation of groundwater flow may result in wider spreading of the pollution plume.

On the basis of the hydraulic conductivity and the hydraulic gradient the effective porosity has been set to 0.33 and the average linear groundwater pore flow velocities have been set to 50 $m \cdot y^{-1}$ for the glaciofluvial sand and 10 $m \cdot y^{-1}$ for the micaceous sand [11].

Average annual precipitation has been set between 700 to 900 $mm \cdot y^{-1}$. Rainwater infiltration into the groundwater system is about half of the annual average; 400 $mm \cdot y^{-1}$ [3].

To estimate the groundwater level more than 100 hydraulic heads have been measured every six weeks from August 1992 to December 1993. This measurement shows that the water level is about 1 m to 3 m below the ground surface. The hydraulic heads annual fluctuation is about 1 m but overall flow direction and gradient remain the same. Therefore the system is considered to be at steady-state [3]. This measurement has been done outside the landfill area respective in two lines heading northwesterly from the landfill.

Directly below the landfill the groundwater level is influenced by a local water table mound formation which is seen from the isopeotential curves in the Figure 5.5. The water table mound underlies the "dome-shaped" eastern part of the landfill and the "original" groundwater surface sloping to the north- west [37].

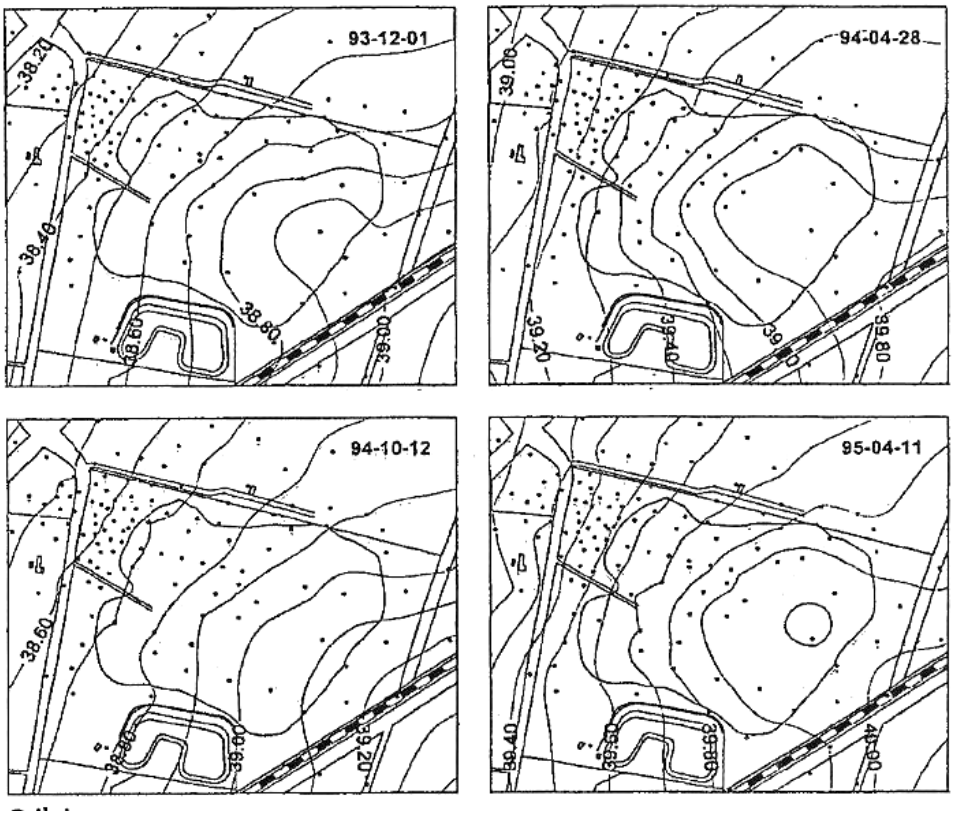


Figure 5.5 - Isopotential curves in the Grindsted landfill area during period from December 1993 to April 1995 [37]

This water table mound formatting has been observed also at other landfills. However the reason for the water table mound formation at the Grindsted landfill has not been finally proven yet. There exist three possible explanations: 1) higher infiltration in this part of the landfill; 2) lower hydraulic conductivities in the aquifer underlying this part of the landfill; 3) higher infiltration in the border regions of the "dome-shaped" area [37].

The first possibility - higher infiltration - does not seem likely. The top soil cover of the landfill is not as sandy as in the surrounding areas, the vegetation seem less dry in the summer season than in the surrounding areas, higher evaporation and therefore lower infiltration is expected at the landfill top cover.

The second possibility - lower hydraulic conductivities - seems more likely to happen because of following reasons. Geological setting beneath the landfill can be different from the surroundings. Simple measurement of the water recharge into the profile wells indicates that the hydraulic conductivities were lower than downstream the landfill (more measurement are needed to ensure the hydraulic conductivity spatial differences). Also growth of bacteria degrading the organic matter may reduce sand pore space as well as methane or carbon dioxide bubbles which are produced during anaerobic degradation process; both these possibilities can also reduce the hydraulic conductivity.

The higher infiltration in the border of "dome-shaped" area due to interflow has been observed at many landfills. The interflow is caused by less permeable layers within waste. The laboratory measurement of the hydraulic conductivity of the waste disposed in the industrial area showed very low conductivity; it is in range of $1.4 \cdot 10^{-7}$ to $8.3 \cdot 10^{-7}$ $m \cdot s^{-1}$ while top soil cover hydraulic conductivity has been measured as $1 \cdot 10^{-4}$ $m \cdot s^{-1}$. After heavy rains interflow at the slopes of the landfill may occur because part of the rainwater will run off down the sloping soil cover on the top of the low permeable industrial waste. Interflow is not expected to happen during warmer period of year because the infiltration in this period is generally low. This phenomena is supported by the groundwater table measurement in the well at the western border of the landfill. The measurement results are shown in the Figure 5.6.

The measurement has taken place during period from October 1994 to September 1995. The groundwater level elevation and the daily precipitation have been measured. There have been observed big differences in the groundwater level elevation during the measurement period (one year). The surface level is 39.9 m which signifies that unsaturated zone thickness varies from 0.1 m to 1.6 m during a year. It is also possible to see small peaks in the groundwater table elevation which appear following days with high precipitation; especially in autumn and winter when the groundwater table is rising. In the late summer and early autumn no peaks or very small peaks were observed [37].

Locally higher infiltration due to presence of interflow (in combination with lower hydraulic conductivities) cause locally higher gradient of the groundwater table and the water table mound may be formed. Anyway further investigations are necessary to fully document the reasons of the water table mound formatting.

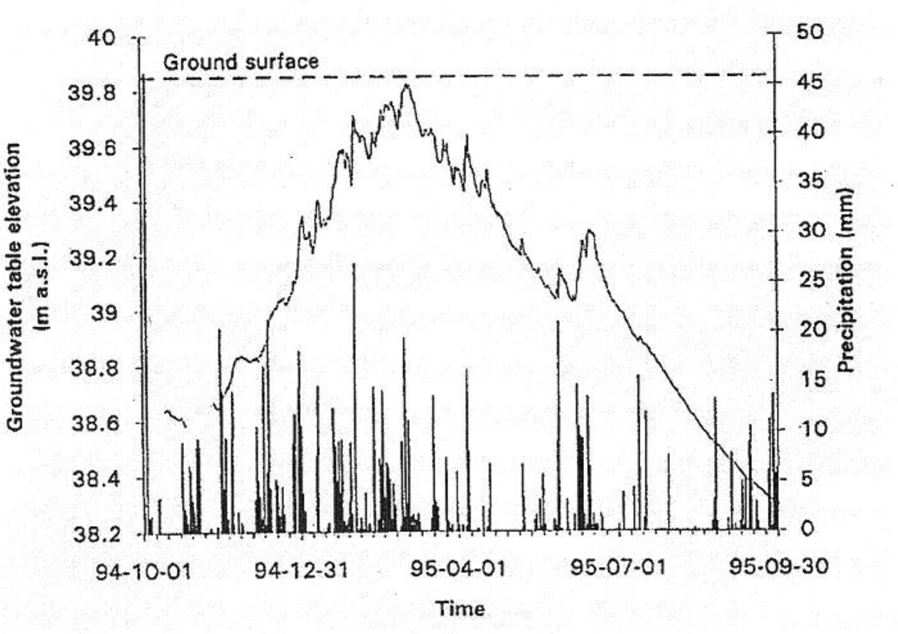


Figure 5.6 - Groundwater level elevation and daily precipitation (black columns) [37]

5.5 Leachate Strength

There have been taken 52 samples from 31 installed leachate wells in order to determine the leachate strength from different areas of the landfill. On the basis of leachate strength the landfill has been at first divided into four areas: 1) a strong leachate area (presents 7 % of the landfill); 2) a medium leachate area which surrounds the strong leachate area (presents 20 % of the landfill); 3) a medium leachate area at the sound of the landfill (presents 10 % of the landfill); and 4) a weak leachate area (presents 63 % of the landfill) [38]. The sketch of the areas location is shown in the Figure 5.7.

This initial classification was primarily based on indicator parameters chloride, ammonia, and NVOC. The average concentrations for each leachate area, number of taken samples, average pH, and average specific conductivity are given in the Table 5.1.

There have been observed large differences for majority of the parameters. The average concentrations of the strong leachate area are 20 to 40 times higher than the weak leachate concentrations.

The strong and the north medium leachate areas correspond with location of industrial waste (lagoon) disposed from 1969 to 1973. The leachate is considered to be in methanogenic phase but significant influence of industrial waste has been observed (high BOD/COD ratio, high sulfate and chloride concentrations). On the other hand ammonia concentration has been observed in typical range for methanogenic landfills. [38].

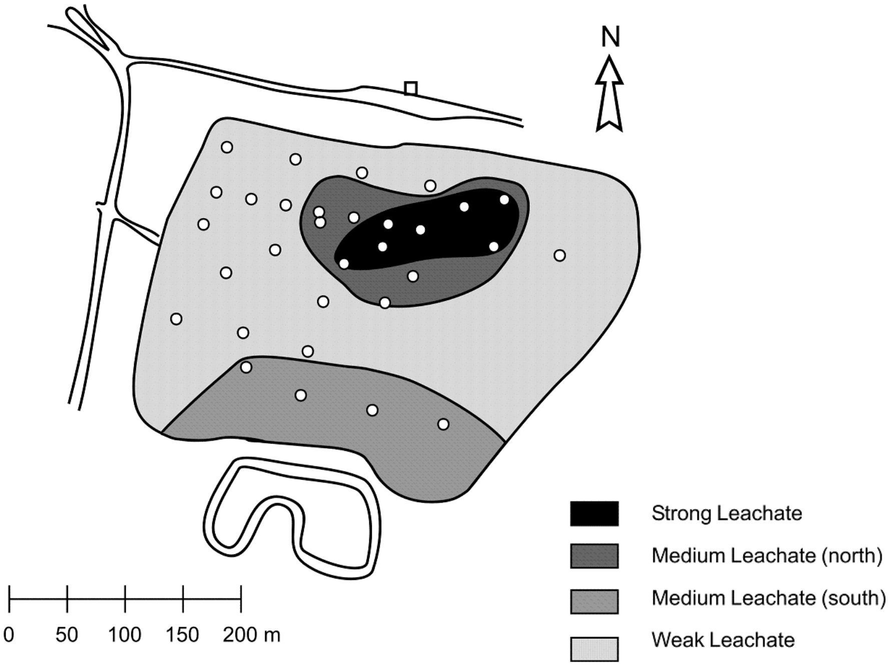


Figure 5.7 - Division of the landfill into four areas according to strength of the leachate [38]

Table 5.1 - Overview of average values for the four leachate areas

Parameter	Strong leachate	Medium leachate (north)	Medium leachate (south)	Weak leachate
Spec.cond.[mS/m]	907	285	231	124
pH [-]	7.01	6.84	5.94	6.2
Chloride [mg/L]	1319	207	464	48
Ammonia [mg/L]	610	215	79	34
NVOC [mg/L]	958	223	99	43
BOD/COD [-]	0.23	0.14	0.02	0.04
Methane [mg/L]	15	15	11	8

Concentrations of the northern medium leachate have been in general 2 to 10 times lower than in the strong lechate area [38]. However the same methane concentration has been observed which indicates stable methanogenic formation. BOD/COD ratio is in the high end of typical methanogenic leachate value.

The medium leachate area in the south coincides with disposal of municipal solid waste at the end of landfill operation in the years 1976 and 1977. Very low BOD/COD ratio and sulphate concentration has been observed. Methane concentration has been observed lower than in the strong and the medium northern leachate. This indicates unstable methanogenesis [38].

The leachate strength of the weak leachate area is generally low. All showed parameters are lower than in the others areas [38].

5.6 BTEX Investigation

In the 1990's the survey was focused on BTEX investigation. Contour maps for benzene, toluene, ethylbenzene, m/p-xylene, o-xylene, and for total BTEX have been constructed. They are available in the Figure 5.8.

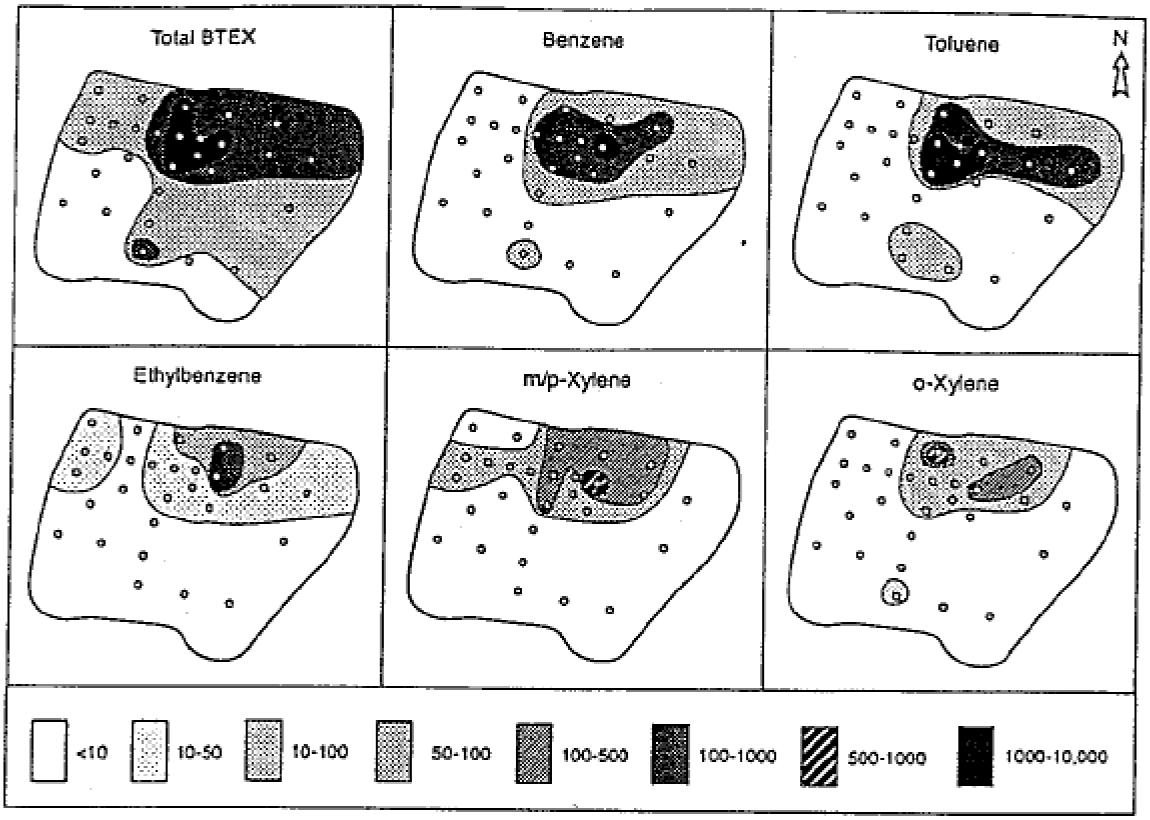


Figure 5.8 - Concentration contour maps for benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene and for total BTEX. Concentrations are given in μg/L.[39]

The contours are made by linear interpolation. The magnitude of the concentrations corresponds with the division of the four leachate areas. High concentrations of total BTEX were found in the north-eastern part of the landfill (area with industrial waste disposal). There were observed very large differences between leachate concentrations in the strong leachate (industrial waste) area and weak leachate area. The total BTEX in the weak leachate area was in majority of places below 10 μg/L and in some place even below 1 μg/L, while the highest measured value in the strong leachate area was larger than 15 000 μg/L. It corresponds to a factor from 100 to 1 000 in averages between the weak and the strong leachate area concentrations [39]. In the medium leachate area only slightly elevated concentrations of BTEX were observed. It probably reflect the BTEX content in the waste disposed here (mainly municipal solid waste was disposed in this area).

The plots of each individual compounds show differences in percentage contribution of each hydrocarbon to the total BTEX content from place to place. Toluene was dominant compound in the south-west part of the strong leachate area or area with the industrial waste disposal, while ethylbenzene was the major compound in the north area. It reflects the differences in the hydrocarbons content in the industrial waste disposed in this area [39].

These are data available for BTEX leachate concentrations. The knowledge of the variability of leachate strength is very important for understanding of groundwater pollution plume formation.

6. CHEMICALS OF CONCERN

6.1 Introduction

As mentioned above different waste has been disposed at the landfill. The most problematic is the waste from pharmaceutical company producing sulpho-drugs, vitamins, and similar products. It is supposed that this waste contains high concentrations of pharmaceutical compounds, respective sulfonamides and barbiturates. The groundwater taken during field work has been analysed for the presence of sulfonamides and barbiturates. The samples were analyzed for the presence of suspected pharmaceutical compounds: dapsone, sulfadiazine, sulfathiazole, sulfamerazine, sulfamethiazole, sulfamethazine, sulfadoxine, sulfamethoxazole, sulfanilic acid, sulfanilamide, and sulfaguanidine from the group of sulfonamides and barbital, amobarbital, butabarbital, pentobarbital, and secobarbital from the group of barbiturates. The risk assessment is focused mainly on these pharmaceutical compounds. Pharmaceutical compounds as groundwater or surface water pollutants have not been investigated too much because it was never considered that these compounds as drugs can contaminate the environment. This is a new thing in the fate and transport modeling of contaminants movement in soil, groundwater and surface water.

The previous survey in 1990ties has been focused on investigation of BTEX (benzene, toluene, ethylbenzene, and xylenes - m-xylene, o-xylene, p-xylene); it has been realized that they are presented in high concentrations. These compounds are also investigated in this survey to find out temporal changes.

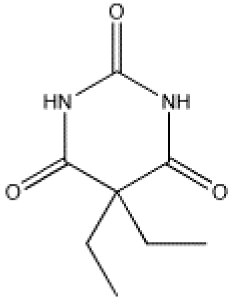
The last group of chemicals of concern are chlorinated compounds respective chlorinated ethanes: 1,1-dichloroethylene, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, trichloroethylene, tetrachloroethylene, and vinyl chloride.

These three groups of compounds were investigated during risk assessment of the Grindsted landfill. Basic information about compounds of interest was summarized. Those are information about their CAS number, molecular formula and structure and parameters which are the most important for the environmental risk assessment. These parameters were reported in special data sheets. Structure of these data sheets were designed directly to the purpose of the environmental risk assessment and can be followed (or used in case of environmental risk assessment of the same compounds) for environmental risk assessment generally. In the Table 6.1 an example of data sheet for barbital is shown; data sheets of the others compounds are available in the Appendix B.

Following captures contain more information about each group of chemicals.

Table 6.1 - Example of the data sheet for barbital

BARBITAL
CAS No.: 57-44-3
Molecular formula: $C_8H_{12}N_2O_3$
Molecular structure:



	Parameter	Importance
Dissociation	$pK_a = 8.14$ (15°C) $^{\text{A) EXP}}$	Mainly in dissociated form $^{\text{D)}}$ ($\alpha_{\text{non-dissociated base}} = 0.00072$)
Volatility	$K_H = 3.61 \cdot 10^{-13}$ atm·m^3/mol $^{\text{A) EST}}$	$K_H < 3 \cdot 10^{-7}$ => less volatile than water (essentially not-volatile from water) $^{\text{D)}}$
Sorption	$K_{oc} = 20.1$ $^{\text{B) EST}}$	K_{oc} is in range of 0 - 50 => very large mobility in soil $^{\text{D)}}$
Bioaccumulation	log $K_{ow} = 0.65$ $^{\text{A) EXP}}$ $K_{ow} = 4.47$	Log $K_{ow} < 3$ => potentially not bioaccumulative $^{\text{D)}}$
Biodegradability	k = from 0 to $4.7 \cdot 10^{-3}$ [d^{-1}] $^{\text{C) EST}}$	From persistent to inherent $^{\text{C)}}$ Not ready biodegradable $^{\text{B)}}$
Ecotoxicity	LC50 = 1162 mg/L (fish, 96-hr) $^{\text{B) EST}}$	
Classification	No data	

Sources: $^{\text{A)}}$ SRC (Syracuse Research Corporation) physprop database: http://www.syrres.com/esc/physdemo.htm
$^{\text{B)}}$ EPI (Estimation Program Interface) Suite $^{\text{TM}}$
$^{\text{C)}}$ calculated on the basis of EPI (Estimation Program Interface) Suite $^{\text{TM}}$ results
$^{\text{D)}}$ BAUN, A., NYHOLM, N., KUSK, K. O.: Environmental Risk Assessment of Chemicals, Institute of Environment & Resources, Technical
University of Denmark, September 2004

Abbreviations:		
	EXP	experimental data
	EST	estimated dat

Note: the data sheets for all other compounds are available in the Appendix B

6.2 Sulfonamides

Sulfonamides (also called sulfa drugs) are synthetic bacteriostatic antibiotic with a high spectrum against both gram-positive and gram-negative bacteria. Sulfonamides inhibit growth of bacteria in body by interfering with its metabolism. Sulfonamides are used to treat urinary tract infections, leprosy, and fungal diseases (toxoplasmosis). However resistance to sulfa drugs has emerged among many microorganisms (e.g. streptococci, and meningococi) [53].

The parent compound, para-aminobenzenesulfonamide, has been synthesized firstly in 1908. In 1932 it has been discovered that dye Prontosil has antagonistic properties against wide range of bacteria and in 1935 it has been found that the sulfonamide portion of Prontosil molecule was responsible for its antibacterial effect. In 1940 it has been shown that sulfonamide inhibited the action of the physiological substance para-aminobenzoic acid, which bacteria need to synthesize the folic acid that is fundamental in DNA replications. Since sulfonamides becomes in use more than 150 different derivatives have been introduced to the market [56].

The chemical sulfonamide functional group is $-S(=O_2)-NH_4$, a sulfone group connected to an amine group. The general formula is RSO_2NH_2 where R is some organic group. The structure of the group is shown in the Figure 6.1.

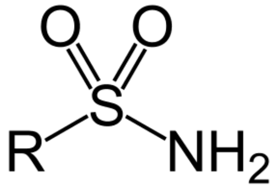


Figure 6.1 - Structure of the sulfonamide group [56]

Most sulfonamides are readily absorbed orally. The main site of absorption is small intestines. However parenteral administration is difficult (soluble sulfonamide salts are alkaline and irritating to tissues). Sulfonamides bind to plasma proteins and are widely distributed in all tissues. High levels are achieved in pleural, peritoneal, synovial and ocular fluids. Sulfonamides are metabolized mainly in liver, excretion is primarily renal. If sulfonamides are administered during pregnancy high levels of them are achieved in fetus [53].

The major problem of today is resistance of organisms to sulfonamides. The resistance may results from random mutation or plasmid-mediated transfer of mutation. Sulfonamides show cross-resistance among its class though no cross-resistance of other antibiotic classes has been shown. There exist many ways how bacteria can develop the resistance therefore the use of sulfonamides as drugs is declining (it is still used for treating of urinary tract infections or for other purposes in combination with other drugs).

Fate and transport of sulfonamides in the environment has not been investigated very much. Only few studies were conducted concerning this topic. Potential toxicity for plants and aquatic organisms was realized. The greatest potential environmental damage discovered yet is the resistance. Indications of increased bacterial resistance in waste effluent from hospitals and pharmaceutical plants have been reported [13].

According to investigation of sulfonamides behavior in human bodies the environmental fate can be forecasted. Sulfonamides absorb to plasma protein and are also widely distributed to all tissues. Therefore distribution of sulfonamides in the subsurface is supposed. However partial absorption can be supposed too.

Following ecotoxicological data were gathered: K_{oc} values vary from 10 to 1 270 which means from very large to low mobility in soil. This ecotoxicological data support the theory converted from human body tissues behavior. All log K_{ow} values are low; lower than 3 which mean they are not potentially bioaccumulative. All sulfonamides log K_{ow} values are below one.

As it was supposed K_H values are also very low (in ranges 10^{-10} to 10^{-15}) so they are much less volatile than water; it means sulfonamides stay in water solution and do not evaporate.

Concerned to biodegradation all sulfonamides were (according to available information) classified as persistent. Persistency is very bad feature for the environment because these compounds do not degrade and they are moving through environmental compartments unchanged and remain in the environment long time. The only slow down process in the subsurface is supposed to be sorption to soil particles.

6.3 Barbiturates

Barbiturates are groups of drugs called as central nervous system (CNS) depressants. They are also known as sedative-hypnotic drugs. Barbiturates produce wide spectrum of CNS depression from mild sedation to anesthesia and therefore are used as sedatives, hypnotics, anesthetics, and anticonvulsants. Sometimes they are also used to treat insomnia but generally this administration has been replaced by safer drugs. The main difference among numbers of the barbiturates drugs is how fast they produce an effect and how long the effect lasts. Barbiturates are classified as ultrashort, short, intermediate, and long-acting. Barbiturates in high concentrations can cause death.

Barbiturates are derivates of barbituric acid which has been discovered in 1863. In 1903 the first medicinal barbiturate - barbital- has been synthesized from the barbituric acid. Since that time barbiturates have been used for medical purposes. More than 2 500 barbiturates have been synthesized and about 50 have been marketed for human use. Barbiturates were very popular in the first half of the 20th century. In 1950s and 1960s reports about their side effects and dependence appear increasingly. From 1970 barbiturates used is regulated by acts.

Barbiturates can be administrated orally, intravenously, and intramuscularly. Absorption occurs very rapidly. About 30 to 40 % are bound to plasma protein and the rest is distributed to the liver and adipose tissue where they become inactivated [7].

The general chemical formula is R-$H_2N_2O_3$. The chemical structure is in the Figure 6.2.

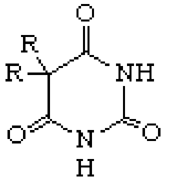


Figure 6.2 - General barbiturates structure

The fate and transport of barbiturates in the environment is unknown. According to available materials no research on this topic has been done yet.

Anyway there can be done an assumption according to their behavior in human bodies. Barbiturates absorb very rapidly to plasma protein and are not distributed widely. This can support theory that barbiturates will not move in the subsurface very fast and they will have tendency to sorb to soil particles.

On the other hand following ecotoxicological data were gathered: K_{oc} values for selected barbiturates vary from 20 to 211 which mean they have very large to medium mobility in soil. According to this they do not tend to sorb to a solid phase and they have the tendency to move with the groundwater flow. So this ecotoxicological data shows directly the opposite behavior than the supposed environmental behavior according to human body tests. However I would support the theory based on K_{oc} values because the K_{oc} value is the coefficient which describes the mobility in the soil.

All log K_{ow} values are low; lower than 3 which mean they are not potentially bioaccumulative. The highest log K_{ow} has pentobarbital 2.1 the lowest barbital 0.65.

As it was supposed K_H values are also very low (in ranges 10^{-13} to 10^{-15}) so they are much less volatile than water; it means sulfonamides stay in water solution and do not evaporate.

Concerned to biodegradation barbiturates were (according to available information) classified from persistent to inherent. So no or very low degradability can be supposed. Persistency is very bad feature for the environment because these compounds do not degrade and they are moving through environmental compartments unchanged and remain in the environment long time. The only slow down process in the subsurface is supposed to be sorption to soil particles.

6.4 BTEX

BTEX is common abbreviation for benzene, toluene, ethylbenzene, and xylenes (ortho-xylene, meta-xylene, and para-xylene). These are compounds with a molecular structure based on the benzene ring. C_6H_6 - benzene molecule consists of six hydrogen's atoms and six carbon's atoms in a cyclical form. The carbon atoms in benzene ring are capable to bond a functional group so isomer creating is possible. More functional group bonding may results in ortho-, meta-, and para- isomers in case of xylene.

BTEX are elemental part of petroleum and related products. Common source of BTEX groundwater pollution are spills and accidental releases of petroleum or gasoline. There are studies documented that this contamination was found at 40 % or 65 % of petroleum hydrocarbon sites. Therefore BTEX fate and transport in groundwater is investigated quite well.

BTEX are considered to be LNAPL (light non-aqueous phase liquids). This means liquids immiscible with water and with lower density than water. If this kind of compounds enter the soil it goes down trough unsaturated zone until they reach groundwater level. On the groundwater surface they form a pancake and moves with a direction of groundwater flow [8].

K_{oc} values of BTEX group vary from 37 for toluene to 520 for p-xylene; it means mobility in soil varies from very large to low.

Log K_{ow} for benzene and toluene is lower than 3 which mean these compounds are potentially not bioaccumulative. Ethylbenzene and xylenes have log K_{ow} higher than 3 which present potential for bioaccumulation. On the other hand all bioconcentration factors (BCF) for ethylbenzene and xylenes are lower than 100 which mean no bioaccumulation. For a conservative assessment I would suggest to consider these compounds as low bioaccumulative.

Concern to biodegradation all compounds are ready biodegradable except of benzene which is considered to be not ready biodegradable.

Naturally all these compounds are volatile in aqueous solutions ($K_H > 1 \cdot 10^{-3}$). So these compounds tend to evaporate from water.

6.5 Chlorinated Compounds

As mentioned above the chlorinated compounds respective chlorinated ethanes investigated at the landfill are 1,1-dichloroethylene, cis-1,2-dichloroethylene, trans-1,2-dichloroethylene (DCE's), trichloroethylene (TCE), tetrachloroethylene (PCE), and vinyl chloride (VC). These compounds generally belong to group of halogenated hydrocarbons with aliphatic structure and with one or more chlorine atom as halogen atom. Halogenated hydrocarbons in general are one of the largest groundwater contaminants. Large quantities of halogenated ethenes were found in groundwater close to industrial sites where solvents, cleaners, and detergents are used.

TCE and PCE are solvents used in dry cleaning and metal degreasing. PCE is furthermore used in manufacture of print removers and printing inks and to remove soot from industrial boilers. DCEs are used to manufacture vinyl chloride. Vinyl chloride is used in the manufacture of polyvinyl chloride.

K_{oc} values for chlorinated compounds vary from 23.7 for VC to 210 for TCE; that presents very large to medium mobility in soil.

Bioaccumulation of the compounds of this group is generally not expected except TCE and PCE where BCF higher than 100 and log K_{ow} higher than 3 respectively was estimated. For TCE and PCE the bioaccumulation is expected to be low to moderate. Bioaccumulation for rest of the compounds (DCEs and VC) is not expected.

Naturally also these compounds are volatile in aqueous solutions ($K_H > 1 \cdot 10^{-3}$).

Common degradation pathway of these compounds is that PCE degrades to TCE, TCE degrades to DCEs and DCEs degrades to VC. For scheme see the Figure 6.3. The biotransformation process occurring is called reductive dechlorination. It is an anaerobic process. The dechlorination of PCE and TCE usually results in cis-1,2-DCE. Therefore the pathway to trans-1,2-DCE and 1,1-DCE is depicted by dashed line [8].

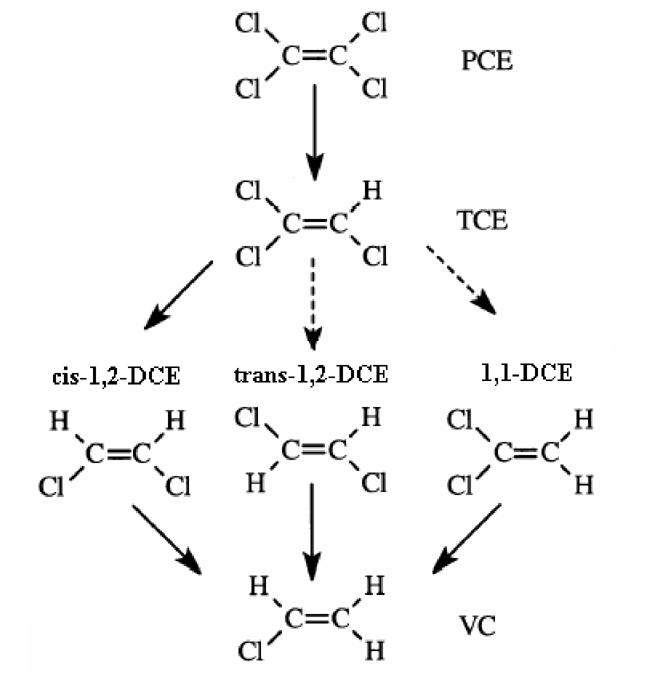


Figure 6.3 - Degradation pathways of chlorinated ethanes [8]

7. PRACTICAL SURVEY

7.1 Field Work

7.1.1 Introduction to the Field Work

Field work is an inherent part of contaminated sites research generally; so it is one of the main and very important tasks of this survey. During field work it is necessary to gain as many data as possible. These data are fundamental for any other research including fate and transport modeling and risk assessment. Quality of the data influences other research significantly; therefore it is necessary to plan and make the field work very carefully and precisely.

The main plan of this field work has been to check old wells (if they are still working), take groundwater samples and soil samples, and if necessary install new wells. It was planned to take at least five groundwater samples and two soil samples from three different depths in the hot spot area of the landfill.

7.1.2 General Description of the Field Work

First field work was done on 27th of September 2005. It was planned to find leachate wells at the hot spot area. They have not been used for many years so it was necessary to check its condition and mark them again. It has been found 7 leachate wells - L9, L12, L13, L14, L29, L30, and L31 but some of them were blocked and it was not possible to get through the well to the groundwater level. It was also planned to take groundwater samples. Unfortunately it was not possible because it was after dry season of the year and there was no groundwater in the wells.

Second field work was done from 24th to 26th of January 2006. The purpose was to take groundwater and soil samples. The plan was to take samples from already installed wells and if it is not possible to install new wells. It was planned to look for the rest of the leachte wells in hot spot area which have not been found last time. It has been found three more wells - L6, L11, and L15; so the only leachte well in hot spot area which has not been found is L16.

Depth and groundwater level of all the wells have been measured; the results of the measurement are listed in the Table 7.1.

Table 7.1 - Wells parameters

Well No.	Well depth (m)	Groundwater level (m)
L6	12.5	4.3
L9	5.7	5.2
L11	15.5	4.8
L12	10.5	7.2
L13	5.4	5.3
L14	8.2	7.9
L15	8.4	6.7
L29	3.0 (probably blocked)	no water detected
L30	2.0 (probably blocked)	no water detected
L31	5.4	4.2

The water samples have been taken from wells L6 and L12. From the other wells it was not possible to take water samples. Wells L29 and L30 seem to be blocked and even if it looks like the other wells provide enough of groundwater (except of well L13 where has been measured only 10 cm of water) it was not possible to pump the water up. So it was necessary to install new wells. New wells have been constructed from ¾ inch metal pipes with a screen at the bottom (as the old wells) rammed into ground by pneumatic hammer. It has been decided to install new wells close to wells L29, L13, and L14. New well L13N has been installed just 1.5 m to the south from the old one, L14N has been installed 6 m to the north from the old one, and L29N has been installed 4.5 m to the north from the old one. The parameters of the new wells are listed in the Table 7.2.

Table 7.2 - Parameters of the new wells

Well No.	Well depth (m)	Groundwater level (m)
L13N	8.0	no data*
L14N	8.2	8.0
L29N	7.0	5.6

*It was not possible to go down with the water-level measuring equipment - probably the pipe was bent during ramming.

7.1.3 Sampling

It was necessary to use different systems for groundwater sampling. For samples which have been analyzed for pharmaceutical compounds (barbiturates and sulfonamides) which are not volatile the vacuum pump was used. But for samples which have been analyzed for volatile compound such as BTEX and chlorinated compound it was not possible to use vacuum system because all volatile compounds would be sucked by the pump. Special system was used for this sampling. The system is described in details in the Appendix C.

The samples were collected and preserved according to their analysis purpose. The samples for sulfonamides and barbiturates analysis were kept cooled (the temperature may not exceed 10 °C). These samples were sent to the laboratories Analycen A/S to do the analysis. BTEX, ammonia, and NVOC samples were preserved by acid. The acid was added in order to lower pH below 2. Samples for BTEX and ammonia were preserved by sulfuric acid (H_2SO_4). BTEX samples were moreover capped with rubber leakless caps to prevent volatilization. Samples for NVOC analysis were preserved by hydrochloric acid (HCl). Samples for chloride analysis were kept frozen.

Specific conductivity, pH, and temperature of each groundwater sample were measured. The results of the measurement are listed in the Table 7.3.

Table 7.3 - Results of pH, specific conductivity, and temperature measurement

Well No.	pH	Specific conductivity (mS/cm)	Temperature (°C)
L6	7.6	2.38	2.1
L12	6.77	2.56	6.0
L13N	5.16	0.663	1.2
L14N	7.9	2.02	8.0
L29N	6.7	2.58	4.9

Soil samples were taken with a special drilling tool close to wells L13N (about 1m to the north-west from the well) and L29N (about 0.5 m to the east from the well). Soil samples from three different depths at the both locations were taken. For detailed information see the Table 7.4.

Table 7.4 – Depths and names of soil samples

Sample name	Depth [m]
S13.1	1.0 - 1.2
S13.2	1.2 - 1.4
S13.3	1.4 - 1.5
S29.1	1.0 - 1.3
S29.2	1.5 - 1.8
S29.3	2.0 - 2.2

Soil samples were put into special nylon bags, closed tightly, placed into glass bottles, kept closed and cooled.

7.2 Samples Analyses

7.2.1 Groundwater Samples Analyses

Groundwater has been analyzed for the presence of pharmaceutical compounds (barbiturates and sulfonamides), BTEX, chlorinated compounds (DCE, TCE, PCE, VC), ammonium, NVOC, and TOC.

Pharmaceutical compounds were analyzed by the company Analycen A/S in Fredericia (Denmark). The method used for the analysis was LC/MS/MS (liquid chromatography/ mass spectrometry/ mass spectrometry). BTEX and chlorinated compounds were analyzed by GC/MS (gas chromatography/ mass spectrometry) analysis. NVOC and TOC were determined via instrument Shimadzu TOC 5000A with autosampler ASI-5000. The amounts of ammonia in the samples were analyzed by autoanalyzer system AA3 which was connected to a computer using AACE software. The method used for the ammonia analysis was salicylate method.

More information about the individual analyses is available in the Appendix D.

7.2.2 Soil Samples Analyses

Before any analyses of the soil samples it is necessary to homogenize them to ensure homogeneity of the samples. It means to mould them by hands. While homogenizing, the samples were kept in plastic bags to prevent evaporation of volatile compounds.

First step of soil samples analysis is to determine water content of the soil samples. For this purpose 5 g of each sample was taken, put into glass vessel and heated up to 150°C for 24 hours. Afterwards the samples were weighted again and water content was calculated. Results are shown in the Table 7.5.

Table 7.5 - Water content of soil samples

Sample	Wet mass [g]	Dry mass [g]	Water amount [g]	w* (%)
S13.1	5	4.14	0.86	21
S13.2	5	3.81	1.19	31
S13.3	5	3.71	1.29	35
S29.1	5	2.73	2.27	83
S29.2	5	2.91	2.09	72
S29.3	5	3.43	1.57	46

*w...water content

Soil samples were also run on GS/MS. Unfortunately there is not possible to make calibration standards and consequently it is not possible to quantify the amount of compounds in the soil samples. This analysis has been done to get information if all the compounds of concern are presented in the soil and to compare the samples between each other to realize which sample/samples are polluted the most. The results - target responses - of the qualitative analysis are shown in the Appendix E. The target responses show that the sample S29 is more polluted than the sample S13. It was already supposed according to the high concentrations of the contaminants in the well L29.

The soil samples were analyzed for presence of sulfonamides, barbiturates, and chlorinated compounds. It was decided to make one representative sample of samples S13 and S29 for the purpose of these analyses. The representative samples were marked S13R and S29R. These representative samples were sent to the same laboratory as the groundwater samples, Analycen A/S, for analyzing. The S29R sample was analyzed for sulfonamides, barbiturates, and chlorinated compounds and the S13R sample was analyzed only for chlorinated compounds. The method used for the analyses of barbiturates and sulfonamides was again LC/MS/MS, for chlorinated compounds KG.4 method was used. Unfortunately there is not any other detailed information available about the analyses.

Leaching Tests

The leaching tests were done with a purpose to set leaching curves and according to the curves to calculate K_d value for the soil. It was decided to perform batch leaching test. This test is simple and easy to perform. The main principal of the method is to obtain equilibrium between the contaminants in solution and contaminants in soil. The leaching tests were done with cooperation of DHI Water & Environment organization in Hørsholm, Denmark. Their labs and equipment were used for the leaching tests. More information about the leaching tests performing is available in the Appendix D.

8. ANALYSES RESULTS

8.1 Groundwater Analyses Results

Table 8.1 - Results of TOC, NVOC, and ammonium groundwater analyses

Parameter	L6	L12	L13	L14	L29
TOC [mg/L]	148	151	24	129	377
NVOC [mg/L]	130	252	8.3	236	357
NH_4^+-N [mg/L]	125	196	21	97	199

These are measured values of TOC, NVOC, and ammonium in the leachate samples. The concentrations of these measured values are generally high. Anyway the concentrations vary significantly with sampling wells. The concentrations in the well L13 are low in comparison with the others well concentrations. The highest concentrations are measured in the well L29.

However according to [16] and its published overview of leachate composition from several landfills the range of TOC published here is from 30 to 29 000 mg/L. So the concentration of TOC measured in the well L13 is lower than overall range; the concentrations measured in the others wells are at the low end of the range. The range of NH_4-N is published as 50 to 2 200 mg/L. Again the concentration in the well L13 is lower than the overall average and the concentrations measured in the others wells are at the low end of the range.

Table 8.2 - Results of BTEX and chlorinated compounds analyses (µg/L); groundwater quality criteria (µg/L)

	L6	L12	L13	L14	L29	Criteria*
Benzene (µg/L)	18	230	9.40	440	62	1
Ethylbenzene (µg/L)	43	48	7.5	25	14	5
m-xylene (µg/L)	120	120	11	31	43	5
o-xylene (µg/L)	43	30	4.2	12	14	5
Toluene (µg/L)	29	21	11	11	1600	5
1,1-dichloroethylene (µg/L)	<1	<1	<1	<1	<1	1
Cis-1,2-dichloroethylene (µg/L)	32	52	11	3.8	10880	1
Trans-1,2-dichloroethylene (µg/L)	1.7	1.5	1.5	1.8	75	1
Trichlorethylene (µg/L)	5.3	2.0	4.2	2.4	120	1
Tetrachloroethylene (µg/L)	1.4	14	1	2.0	7	1
Vinyl chloride (µg/L)	<1	4.38	<1	<1	600	0.2

* criteria according to [19] for groundwater used as drinking water

As it is seen from the results 1,1-DCE was not detected in any sample so the criterion is met. Vinyl chloride was not detected in wells L6, L13, and L14 but it was detected in the other wells. Especially in the well L29 the measured concentration is really high (3000 times higher than the criterion). For the other compounds the criteria are not met at all. In almost all cases the concentrations are much higher then the limits are. Just in the case of trans-1,2-DCE the concentrations in the wells L6, L12, L13, and L14 are not so high but anyway are higher than groundwater quality criteria.

In general it is possible to say that the most polluted is groundwater in the well L29. Especially the concentration of cis-1,2-DCE is extremely high. Also concentration of toluene in the well L29 is really high. The vinyl chloride concentration in the well L29 is alarming too especially because vinyl chloride is considered to be carcinogenic.

Upper mentioned ecological risks are assessed on the basic of comparison of the measured values to the quality criteria. Another possibility how to assess ecological risk of measured concentrations is to calculate their risk characterization ratio (RCR) according to [6]. RCR serves as a criterion of adverse effects for the environment. It is a ratio between PEC (predicted environmental concentration) and PNEC (predicted no effect concentration).

$$RCR = \frac{PEC}{PNEC}$$

Equation 8.1

Where PEC is the average value measured in all five wells or concentration modeled by the RISC 4 (see Capture 9) and PNEC is calculated on the basis of LC50 or EC50 or NOEC (no observed effect concentration) values and relevant assessment factor. If the RCR is lower than 1 there is no risk of adverse effect, if the ratio is higher than 1 there exists a risk of an adverse effect because the predicted concentration in the environment is exceeding the observed no effect level.

Following table shows RCR for BTEX and chlorinated compounds. As a PEC value an average concentration of the five measured concentration was taken.

Table 8.3 - RCR for BTEX and chlorinated compounds

	PEC [µg/L]	LC50 [mg/L]	PNEC [µg/L]	RCR [-]	Potential of effect
Benzene	151.88	20	20	7.60	**yes**
Toluene	334.4	4.3	4.3	77.77	**yes**
Ethylbenzene	27.5	42.3	42.3	0.65	no
m-xylene	65	3.7	3.7	17.57	**yes**
o-xylene	20.64	1.3	1.3	15.88	**yes**
1,1- DCE	<1	224	224	<1	no
Cis-1,2-DCE	2195.76	2.08	2.08	1055	**yes**
Trans-1,2- DCE	16.3	2.08	2.08	7.84	**yes**
Trichlorethylene	26.78	2	2	13.39	**yes**
Tetrachloroethylene	5.08	5	5	1.02	**yes**
Vinyl chloride	120.876	2.32	2.32	52.10	**yes**

The table shows that in all cases except ethylbenzene and 1,1-DCE the RCR ratio is higher than one. It means this average concentrations present risk for the environment respective groundwater. In case of ethylbenzene the average concentration does not present potential adverse effect for the environment but if the highest measured concentration is selected, 48µg/L, the RCR ratio is 1.13 which is higher than one. It could be said that concentration found in the groundwater for ethylbenzene also present a risk for the environment. 1.1-DCE has not been detected in groundwater at all so it does not pose any risk.

The following table shows measured concentrations of barbiturates and sulfonamides.

Table 8.4 - Results of pharmaceutical compounds analyses - barbiturates and sulfonamides (μg/L)

	L6	L12	L13	L14	L29
Barbital (μg/L)	250	100	13	130	0.68
Amobarbital (μg/L)	340	470	94	310	1.3
Butabarbital (μg/L)	64	100	<5	35	0.048
Pentobarbital (μg/L)	130	130	20	340	0.43
Secobarbital (μg/L)	9	18	4	13	<2
Dapsone (μg/L)	<1	<1	2	<1	<1
Sulfadiazine (μg/L)	450	380	31	51	2500
Sulfathiazole (μg/L)	47	92	17	58	4300
Sulfamerazine (μg/L)	800	770	43	220	3000
Sulfamethiazole (μg/L)	790	620	18	130	3100
Sulfamethazone (μg/L)	870	1100	270	4000	7600
Sulfadoxine (μg/L)	<1	<1	<1	<1	<1
Sulfamethoxazole (μg/L)	<1	<1	<1	<1	<1
Sulfanilic acid (μg/L)	56000	3300	380	1800	83000
Sulfanilamid (μg/L)	270	360	15	6700	2000
Sulfaguanidine (μg/L)	3400	5600	210	5700	18000

Sulfadoxine and sulfamethoxazole were not detected in any sample. Dapsone was detected only in the well L13 but in low concentration. The other compounds were detected at all samples. In some cases very high concentrations of the compounds were found - sulfuric acid in the well L29 or in the well L6, sulfaguanidine in the well L29.

There exist no water quality criteria for these compounds so the measured values can not be compared with them. It was again decided to calculate RCR ratio. As a PEC average concentration of the all measured values was taken. RCR and potential of adverse effect are shown in the Table 8.5.

Table 8.5- RCR for pharmaceutical compounds

	PEC [μg/L]	LC50 [mg/L]	PNEC [μg/L]	RCR [-]	Potential of effect
Barbital	98.736	1162	1162	0.08	no
Amobarbital	243.06	123	123	1.98	**yes**
Butabarbital	39.8096	272	272	0.15	no
Pentobarbital	124.086	118	118	1.05	**yes**
Secobarbital	8.8	69	69	0.13	no
Dapsone	0.4	3.65	3.65	0.11	no
Sulfadiazine	682.4	7.37	7.37	92.60	**yes**
Sulfathiazole	902.8	3.88	3.88	232	**yes**
Sulfamerazine	966.6	5.52	5.52	175	**yes**
Sulfamethiazole	931.6	4.98	4.98	187	**yes**
Sulfamethazine	2768	4.13	4.13	670	**yes**
Sulfadoxin	<1	8.59	8.59	<1	no
Sulfamethoxazole	<1	4.47	4.47	<1	no
Sulfanilic acid	28896	151	151	191	**yes**
Sulfanilamid	1869	5.78	5.78	323	**yes**
Sulfaguanidine	6582	9.951	9.951	661	**yes**

As the table shows from the barbiturates group only amobarbital and pentobarbital pose risk for the environment. Barbital, butabarbital, and secobarbital average concentrations do not pose risk for the environment. Even if the highest measured value of barbital, butabarbital, and secobarbital are used for RCR calculation the ratios are still lower than one which means these concentrations of the compounds do not pose treat for the environment.

Almost all average concentrations of sulfonamides pose treat for the environment; except those which were not detected at all (sulfadoxine and sulfamethoxazole) and except dapsone which was detected only in one well in really low concentration (2μg/L). All the others RCR are far higher than one. But it is also necessary to keep in mind that the LC50 values used are estimated values by EPI so they are not completely sure.

8.1.1 Objectiveness of the Analyses Results

There were taken groundwater samples from five selected points of the landfill. It was decided to take samples from five different points in order to keep the survey objective. As it is possible to see from the analyses results some wells are much more polluted than the others. If there was taken only one sample the survey will not be objective. Five samples are enough to make the survey objective and to have knowledge about the groundwater pollution bellow the landfill.

For the RCR calculation the average values of the measured concentrations from the five wells were used. It is supposed that the water is mixed in the subsurface so using the average measured concentration is reasonable and reflects the reality the most.

For the purpose of the risk assessment the field survey was adequate and provided enough data to evaluate the ecological risks.

8.2 Soil Samples Analyses Results

Table 8.6 - Results of chlorinated compounds soil samples analyses and soil quality criteria (μg/kg)

Parameter	S13R	S29R	Criteria*
1,1-dichloroethylene (μg/kg)	<50	140	5000
Cis-1,2-dichloroethylene (μg/kg)	<50	50	85000
Trans-1,2-dichloroethylene (μg/kg)	<50	350	85000
Trichlorethylene (μg/kg)	9.7	290	5000
Tetrachloroethylene (μg/kg)	11	37	5000
Vinyl chloride (μg/kg)	<50	340	400

* criteria according to [19] for contaminated soil

Just by comparison of the measured concentrations and the soil quality criteria is obvious that the soil quality criteria are met.

The detection limit for TCE and PCE in soil is 5μg/kg while detection limit for DCEs and vinyl chloride is 50μg/kg (which is quite high value). Probably this is reason why no DCEs and vinyl chloride were detected in the soil sample S13R. On the other hand no DCEs and vinyl chloride were detected in the soil sample S13R leachate (see Table 8.8) so it corresponds with the soil sample analysis. For the higher detection limit of 5μg/kg TCE and PCE in the soil sample S13R were detected. The concentrations of TCE and PCE in the soil are quite low however they are still higher than those found in groundwater sample L13. In the case of TCE the soil concentration is two times higher than concentration found in the groundwater sample (4.2μg/L). Concentration just above the detection limit was found in the groundwater sample in the well L13 for PCE and eleven times higher concentration of PCE was found in the soil sample S13R. In the leachate water of the S13R sample the TCE concentration was found three times higher than concentrations in the soil sample. Opposite situation occur in the case of PCE where the concentrations in leachate are around half of the soil concentration value.

As expected concentrations in the soil sample S29R are much higher than in the soil sample S13R. That corresponds with the groundwater samples too. Quite high concentration of 1,1-DCE was found in the soil sample S29R which was not supposed because there is no concentration of the compound found neither in the groundwater sample nor in the leachate samples. Completely different situation occur in the case of cis-1,2-DCE; there is really high concentration found in the groundwater sample but concentration found in the soil sample is quite low (in fact it is just above the detection limit). On the other hand it is possible to say that the soil sample concentration correspond with leachate concentration of the S29R sample (see the

Table 8.9) which vary from 14µg/L to 52µg/L. Concentration of trans-1,2-DCE is much higher in the soil sample than in the groundwater sample and in the leachate too (actually no trans-1,2-DCE was detected in the S29R leachate sample). Concentration of trans-1,2-DCE in the soil is 4.5 times higher than concentration in the groundwater sample from the L29 well. Similar situation occur in the case of TCE; concentration in the soil is higher than in the groundwater and the leachate. The soil concentration is 2.3 times higher than the groundwater concentration and around three times higher than the highest leachate concentration. Concentration of PCE in the soil is again higher than in the groundwater (seven times) and in the leachate (1.8 times for the highest leachate concentration). Surprisingly vinyl chloride concentration in the soil is really high in comparison with the leachate concentration where the highest concentration is only 9µg/L. This is 38 times lower than in the soil sample. On the other hand in comparison with the groundwater concentration the soil concentration is 20 times lower.

Table 8.7 - Results of pharmaceutical compounds soil samples analyses

Parameter	S29R
Barbital (µg/kg)	563
Amobarbital (µg/kg)	651
Butabarbital (µg/kg)	654
Pentobarbital (µg/kg)	651
Secobarbital (µg/kg)	<10
Dapsone (µg/kg)	44
Sulfadiazine (µg/kg)	84
Sulfathiazole (µg/kg)	860
Sulfamerazine (µg/kg)	660
Sulfamethiazole (µg/kg)	130
Sulfamethazine (µg/kg)	2 400
Sulfadoxine (µg/kg)	10
Sulfamethoxazole (µg/kg)	<10
Sulfanilic acid (µg/kg)	35
Sulfanilamid (µg/kg)	420
Sulfaguanidine (µg/kg)	94

The soil quality criteria for the pharmaceutical compounds is not assessed (the situation is the same as for ground and surface water). The pharmaceutical compounds were never considered to be soil pollutants. There is no possibility to calculate RCR ratio because the ratio is concerned to the water environment not to the soil. The only possibility how to assess the range of the soil pollution by the pharmaceutical compounds is via water – it means laboratory leaching tests or tests of the groundwater sample (because the soil pollution is supposed to be leached into the groundwater).

8.2.1 Leaching Tests Analyses Results

The leaching tests have been done in order to set soil K_d values. Unfortunately it is necessary to say that the leaching tests were not successful. The leaching tests results vary significantly so it is not possible to draw the leaching curve which is needed to set the K_d values.

It is supposed that the lowest L/S ratio has the highest concentration of contaminants of the sample and with increasing L/S ratio the concentration is decreasing. But as it is possible to see from the results below it does not work so well. Especially the results of leaching tests of the sample S13 do not match this rule at all. The concentrations vary randomly. The situation is little bit better in the case of leaching test of the sample S29 where in some cases the rule works but not for all of the samples. Similar situation occur to the representative samples.

It is supposed that this problem happened because the samples were not homogenous. Each sample was homogenized for 20 minutes but it seems it was not enough.

Because of the data variations the leaching tests results could not be used for the purpose it was done; it was decided to compare the leaching test results with the results of the groundwater samples.

BTEX and Chlorinated compounds - Sample S13

The leachate tests results are shown in the Table 8.8 and discussed bellow.

Table 8.8 - Leaching tests results - BTEX and chlorinated compounds - sample S13, µg/L

Sample	S 13.1			S 13.2			S 13.3			S 13.R		
L/S ratio	2	5	10	5	10	15	2	5	10	2	5	10
Benzene	6.8	<1	18	6.3	2.7	15	3.2	1.9	10	6.8	5.8	16
Toluene	45	49	58	39	49	50	44	42	43	<1	49	52
Ethylbenzene	8.5	8.9	9.6	7.6	9.1	8.7	7.2	8.8	9.5	7.5	7.6	10
m-xylene	10	10	11	8.9	10	10	13	10	11	8.8	9	12
o-xylene	5.4	6.6	8.3	4.4	5.5	6.4	5.4	4.6	1.7	3.6	4.6	5.8
1,1-DCE	<1	187	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cis-1,2-DCE	<1	<1	2.2	<1	1.7	2.6	<1	<1	<1	<1	<1	<1
Trans-1,2-DCE	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
TCE	<1	65	2.7	<1	36	39	<1	<1	<1	43	<1	43
PCE	<1	2.1	4.1	3.2	2.6	5.0	<1	3.7	1.9	<1	5.8	2.5
VC	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

The soil sample S13 leachate concentrations of vinyl chloride correspond with the groundwater concentrations; in both cases the concentrations were below detection limit.

Similar situation occurs to trans-1,2-dichloroethylene. In the leachate the concentration of trans-1,2-dichloroethylene is below detection limit in all tests. In the groundwater samples the measured concentration is 1.5µg/L which is just above the detection limit. The reason why in the groundwater the trans-1,2-dichloroethylene was detected and in leachate it was not can be that majority of the contaminant is already leached into groundwater.

Really strange result is obtained for 1,1-dichloroethylene in the leachte test of the sample S13.1 L/S ratio=5; the value there is 187 µg/L which is really high in comparison that no 1,1-DCE was detected in any groundwater sample. Because this value is really isolated from all the others it is suggested the possibility of random measuring mistake.

Concentrations of cis-1,2-dichloroethylene in the leachate are just above the detection limit or lower then detection limit which means that the concentrations in the leachte are around five times lower (if detected) than the concentration in the groundwater.

PCE was not detected in the groundwater in the well L13 but there were found concentrations from 1.9 to 5.8µg/L in the leachate.

Similar situation occurs in the case of trichloroethylene. There was detected quite low concentration in groundwater but the concentrations in leachte are much higher (in one case 16 times) than the concentration in the groundwater.

The results of chlorinated compounds tests show that the compounds with very large mobility in soil as cis-1,2-DCE are found in higher concentrations in groundwater but the compounds with large (TCE) and medium (PCE) mobility were detected in higher concentrations in leachate water. It could be said that the concentrations in leachate and groundwater corresponds with the mobility in soil - very mobile compounds moves faster in the soil and also go faster to the groundwater and are then found in higher concentration in groundwater than in the leachate.

Concerned to the BTEX group the concentrations in leachate vary greatly and it is difficult to compare them with the groundwater concentrations.

Benzene leachate concentrations vary from not detected (less than 1) to 18µg/L while the concentration found in the groundwater is 9.4µg/L. The situation is similar to o-xylene where concentrations in leachte vary from 1.7 to 8.3µg/L; the concentration found in the groundwater is 4.2µg/L so it is possible to say the average of leachate values.

M-xylene and ethylbenzene leachate concentrations correspond with the concentrations found in the groundwater. There is only small variability of ±2 µg/L for m-xylene between the groundwater sample and all the leachte tests. The range of ethylbenzene concentrations in the leachate is from 7.2 to 10µg/L and the groundwater concentration is 7.5µg/L.

Toluene leachate concentrations are much higher than the concentration found in the groundwater except for the S13.R L/S ratio=2 sample where toluene was not detected. In the other samples the leachate concentrations are up to ten times higher than the groundwater concentration found in the well L13.

In this case is difficult to build any criterion for compounds behavior; as mentioned above the concentrations in leachate vary from lower than in the groundwater to higher than in the groundwater within the same compound.

BTEX and Chlorinated compounds - Sample S29

The leachate tests results are shown in the Table 8.9 and discussed bellow.

Table 8.9 - Leaching tests results - BTEX and chlorinated compounds - sample S29, µg/L

Sample	**S 29.1**			**S 29.2**			**S 29.3**			**S 29.R**		
L/S ratio	**5**	**10**	**15**	**5**	**10**	**15**	**5**	**10**	**15**	**5**	**10**	**15**
Benzene	36	19	19	35	32	36	46	27	22	122	30	30
Toluene	112	39	47	52	7.1	76	74	72	76	157	57	56
Ethylbenzene	426	148	152	248	244	277	35	29	29	161	52	53
m-xylene	499	174	178	291	286	324	252	213	211	1600	522	530
o-xylene	<1	<1	<1	<1	<1	<1	<1	<1	<1	129	42	<1
1,1-DCE	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cis-1,2-DCE	7.9	2.9	2.9	8	6.8	7.9	60	38	32	52	14	15
Trans-1,2-DCE	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
TCE	97	<1	<1	35	60	20	45	42	65	104	24	63
PCE	15	<1	5.4	<1	<1	<1	16	13	13	20	7.4	8
VC	<1	<1	<1	<1	<1	<1	<1	<1	<1	9.0	<1	<1

1,1-DCE was not found neither in the groundwater from the well L29 nor in the leachate of the S29 sample.

Surprisingly no trans-1,2-DCE was detected in the leachate water even if there was detected high concentration of this compounds in the groundwater (75µg/L).

Vinyl chloride was detected only in the S29.R L/S ratio=5 sample; in the other samples it was not detected at all even if really high concentration of vinyl chloride (600µg/L) was found in the groundwater.

In the leachate from the sample S29.2 no PCE was detected while in the others samples the concentrations vary from 5.4 to 20µg/L which is almost three times higher than concentration in the groundwater (7µg/L).

Concentrations of TCE in the leachate were detected in range from 20 to 104µg/L. The lowest leachate value is six times lower than the concentration in the groundwater while the highest leachate value comes near to the groundwater concentration (120 µg/L) but still is lower.

Cis-1,2-dichloroethylene was detected in really high concentration in the groundwater in the well L29; the concentration is 10 880µg/L while the concentration in the leachate were maximally 60µg/L which is far lower.

To conclude the chlorinated compounds results it is possible to say that only PCE was detected in higher concentration in the leachate than in the groundwater, the others compounds were found in higher or much higher concentrations in the groundwater. It corresponds with the compounds mobility - PCE has the lowest soil mobility of these compounds so it stays longer in the soil.

The results for BTEX again vary greatly. For example o-xylene was detected in leachate only in representative sample and furthermore in concentrations much higher than in the groundwater; from three times to nine times.

On the other hand m-xylene was detected in the leachate in much higher concentration, than in the groundwater. Especially in the representative sample its concentration is really high (1 600µg/L) which is 37 times more than the concentration in the groundwater.

Similar situation occur to ethylbenzene – the leachate concentration is from two to thirty times higher than the groundwater concentration.

Benzene leachate concentrations vary from 19 to 46µg/L which is from 1/3 to ¾ lower than the groundwater concentration. Only in the leachate of the S29.R L/S ratio=5 the leachate concentration is two times higher than the groundwater concentration.

Toluene was found in really high concentration in the groundwater - 1 600µg/L; the highest leachate concentration is ten times lower.

It general when the leachate and the groundwater concentration of BTEX are compared it could be said that it meets the rule of mobility in the soil - very mobile or mobile compounds (toluene, o-xylene, and benzene) are detected in higher concentrations in the groundwater while compounds with medium or low mobility (m-xylene and ethylbenzene) are detected in higher concentrations in the leachate (with small exception of benzene concentration in the S29.R L/S ratio=5 sample).

If the results of the leaching tests of the representative samples are compared with the others leaching tests from different depths it supports the theory that the soil samples were not homogenous. The leachate concentrations of representative samples should be in the same range as leachate concentrations of the samples from three different depths. Especially the value of 1 600µg/L for m-xylene in the S29.R sample L/S ratio=5 is completely out of range of the other leaching tests. Similar situation occurs to benzene; its concentration in the representative leachate sample is three times higher than in the samples S29.1,2,3. The toluene concentrations are getting closer (112µg/L in the S29.1) in comparison to the representative sample (157µg/L). Concentrations of ethylbenzene are on the other hand lower - around 2.5 times - in the representative sample. O-xylene was not detected in any of the S29.1,2,3 samples but was detected in the representative sample in quite high concentration of 129µg/L.

1,1-DCE and trans-1,2-DCE were not detected in the representative sample which corresponds to the results of the S29.1,2,3 samples. Vinyl chloride was detected only in the representative sample S29.R (9.0µg/L) which again supports the theory that the samples were not homogenous. The leachate concentrations of cis-1,2-DCE, TCE, and PCE in the representative samples slightly corresponds to the concentrations in the leachate S29.1,2,3 samples.

In the representative sample S13.R the BTEX leachate concentration corresponds to the leachate concentrations in the samples S13.1,2,3.

1,1-DCE, trans-1,2-DCE, and vinyl chloride were not detected in the representative sample as well as in the S13.1,2,3 samples. Cis-1,2-DCE also was not detected in the representative sample but was detected in the S13.1,2 samples. Anyway the leachate concentration of these samples are low (the highest

2.6µg/L) so it is possible to say that the concentrations of the representative sample also corresponds to the samples S13.1,2,3. The range of concentrations of TCE and PCE in the representative sample corresponds to the S13.1,2,3 samples.

It is very difficult to compare the leachate water concentrations and the groundwater concentrations. The results of the leaching tests are random. It seems that the soil samples were very inhomogeneous. Probably different waste was disposed in different layers and this is the reason why the results of the leaching tests differ greatly.

Pharmaceutical compounds - Sample S29R

The leachate tests results are shown in the Table 8.10 and discussed bellow.

Table 8.10 - Leaching test results - pharmaceutical compounds - sample S29R, L/S=5

Parameter	S29R(L/S=5)
Barbital (µg/L)	6
Amobarbital (µg/L)	120
Butabarbital (µg/L)	36
Pentobarbital (µg/L)	48
Secobarbital (µg/L)	<1
Dapsone (µg/L)	<1
Sulfadiazine (µg/L)	15
Sulfathiazole (µg/L)	46
Sulfamerazine (µg/L)	55
Sulfamethiazole (µg/L)	9
Sulfamethazine (µg/L)	150
Sulfadoxin (µg/L)	<1
Sulfamethoxazole (µg/L)	<1
Sulfanilic acid (µg/L)	7
Sulfanilamid (µg/L)	28
Sulfaguanidine (µg/L)	10

The situation of the pharmaceutical compounds leachate concentrations comparison to the groundwater concentrations is similar to BTEX and chlorinated compounds; probably the problem of homogeneity of the sample. However it is possible to find some identical features - dapsone, sulfadoxin, and sulfamethoxazole were not found neither in the groundwater of the L29 well nor in the S29.R L/S ratio=5 leachate sample. On the other hand sulfanilic acid was found in the highest concentration in the L29 well groundwater but the concentration in the leachate belongs among the lowest. In fact the groundwater concentration of sulfanilic acid is more than 10 000 times higher than the leachate concentration. Concentrations of sulfadiazine, sulfathiazole, sulfamethiazole and sulfanilamide in the groundwater are around a hundred times higher than the leachate concentrations, sulfamerazine and sulfamethazine groundwater concentration is around fifty times higher, and sulfaguanidine groundwater concentration is more than a thousand times higher than the leachate concentration.

Barbiturates concentrations in the groundwater from the well L29 are very low; much lower than the concentration of the leaching tests. Only secobarbital was not detected in the leachate water as well as in the groundwater sample L29. Other leachate concentrations are much higher than the groundwater concentrations. The leachate concentration of barbital is ten times higher than the concentration in the groundwater sample L29. The leachate concentrations of amobarbital and pentobarbital are a hundred times higher than the groundwater sample L 29 concentration. The biggest difference among the leachate and the groundwater concentration presents butabarbital which leachate concentration is around a thousand times higher than the concentration measured in the well L29 groundwater sample.

9. GRINDSTED LANDFILL RISK ASSESSMENT

9.1 Introduction to the Modeling

Possible adverse ecological effects of the landfill are contamination of groundwater and surface water. There was also observed volatilization of contaminants from the waste through final soil cover at the landfill. The volatilization is held on open area, the volatilities are spread immediately in the air so there are no dangerous concentrations of volatiles there. The danger of volatilization can be neglected.

The groundwater below the landfill and also farer from the landfill is threatened due to groundwater movement and dispersion. There are two types of aquifer - shallow aquifer (which is threatened for sure) and deep aquifer. The deep aquifer is located below clay/silt layer which is supposed to be impermeable; hopefully the deep aquifer is not contaminated.

The groundwater carries the contamination farer from the landfill in the direction of groundwater flow and there arise a risk of contamination of surface water bodies in the direction of groundwater flow. The previous investigations show that the groundwater flow is northwesterly. In this direction about 2 250 m far from the landfill is a lake. The groundwater is supposed to flow in the direction of the lake. See the

Figure 9.1 it depicts supposed groundwater flow by pink color (the blue lines are groundwater potentiometric curves). According to the groundwater flow direction the lake is threatened by the contaminated groundwater.

The endpoints are selected with respect to the ecosystem potentially at risk and the ecological effects description. There is no doubt about selection of the groundwater as an endpoint; it is contaminated very much. As another endpoint the lake was selected with respect to the groundwater flow. Also river was set as a potential endpoint; it is situated about 2 000 m north from the landfill. Even if the main stream of the groundwater flow was observed northwesterly there exists a danger of contamination of the river due to seasonal variation of groundwater flow.

Here are basic information about the lake and the river. The volume of the lake is 465 000 m^3 with an average depth 1.55 m. The lake is about 2 250 m far from the landfill in northwest direction. The annual average flow-rate is 2 246 L/s. The river is about 2 000 m to the north of the landfill. The cross-sectional area of the river is 11 m^2 and the annual average flow rate is 1 778 L/s. The Appendix F contains monthly flow-rates and a map with highlighted points where the flow data of the river and the lake were measured. Unfortunately there is no information about organic carbon fraction in the sediment and about hydraulic conductivity of surface water bed. Geology and hydrogeology characteristic close to the river and the lake are observed to be the same as beneath the landfill.

The objective of the risk assessment is to model spreading of the compounds through the shallow aquifer, find out if the contaminants can reach the lake and the river; if yes set contaminants concentrations. For the risk assessment and contaminant transport modeling software RISC 4 was used (more information about the software is in the Capture 4).

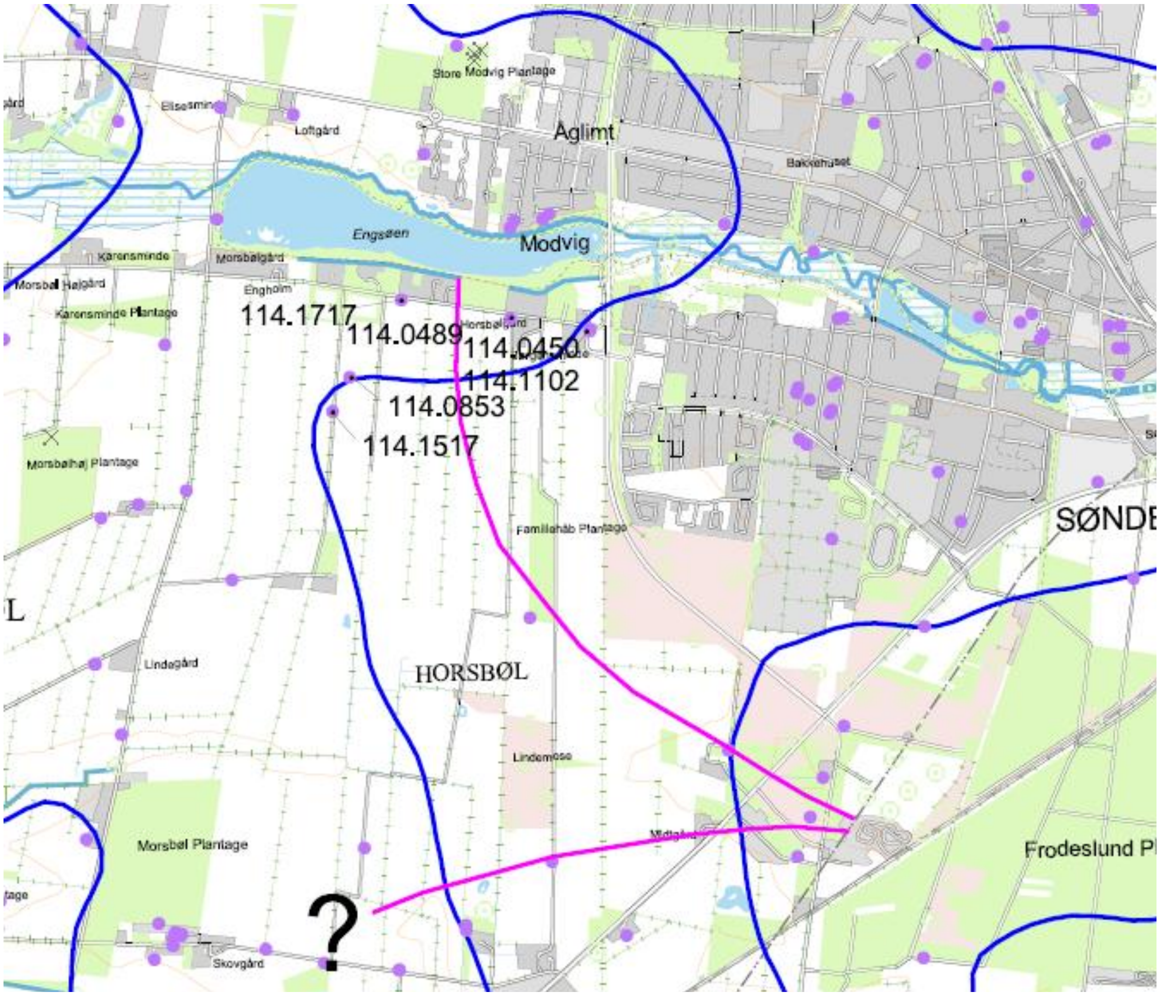


Figure 9.1 - Supposed groundwater flow from the landfill (pink color line)

9.2 Selection of Chemicals for Modeling

There were detected five barbiturates, nine sulfonamides, all BTEX, and five chlorinated compounds in the groundwater samples; it means together 25 compounds. There are problems to model so many compounds; firstly the software for the risk assessment - RISC4 - is able to model only twenty compounds together, secondly if there is too much of results it is confusing and difficult to deal with them. It was decided to select representative compounds from each group - two barbiturates, three sulfonamides, three BTEX, and four chlorinated compounds.

The selection criteria for sulfonamides and barbiturates selection are following - comparison of K_{ow} (reflects the bioaccumulation ability of compounds), K_{oc} (reflects soil mobility of compounds), and K_H (reflects volatility from aqueous solutions) values of all the compounds with combination of concentration found in the groundwater. Following table provides an overview of K_{ow}, K_{oc}, and K_H for barbiturates and sulfonamides (groundwater concentration of these compounds is shown in the Table 8.4) and shows the selected representative compounds – highlighted by bold letters.

Table 9.1 - K_{ow}, K_{oc}, and K_H overview for barbiturates and sulfonamides

	K_{ow}	K_{oc} (according EPI)	K_H (atm·m^3/mol)
Barbital*	**0.65**	**20.1**	**$3.61 \cdot 10^{-13}$**
Amobarbital*	**2.07**	**106**	**$8.44 \cdot 10^{-13}$**
Butabarbital	1.65	62	$6.36 \cdot 10^{-13}$
Pentobarbital	2.1	114	$8.44 \cdot 10^{-13}$
Secobarbital	1.97	211	$8.35 \cdot 10^{-13}$
Dapsone	0.97	$1.27 \cdot 10^{3}$	$3.11 \cdot 10^{-14}$
Sulfadiazine	-0.09	189	$1.58 \cdot 10^{-10}$
Sulfathiazole	0.05	945	$5.85 \cdot 10^{-14}$
Sulfamerazine	0.14	306	$1.75 \cdot 10^{-10}$
Sulfamethiazole	0.54	166	$2.63 \cdot 10^{-14}$
Sulfamethazine*	**0.89**	**496**	**$3.05 \cdot 10^{-13}$**
Sulfadoxine	0.7	99.8	$1.42 \cdot 10^{-15}$
Sulfamethoxazole	0.89	$1.53 \cdot 10^{3}$	$6.42 \cdot 10^{-13}$
Sulfanilic acid*	**-2.16**	**10**	**$8.89 \cdot 10^{-13}$**
Sulfanilamide	-0.62	40.2	$1.5 \cdot 10^{-10}$
Sulfaguanidine*	**-1.22**	**129**	**$1.01 \cdot 10^{-15}$**

*Selected compounds are highlighted by bold letters

Why just these compounds? The criterion was to select compounds with the highest and the lowest K_{ow}, K_{oc}, and K_H values. In all cases the K_H value is very low (far lower than water volatilization); therefore the value of Henry's law constant was neglected from the selection procedure. Anyway it is observed that there are not always selected compounds with the lowest and the highest K_{ow} and K_{oc} values. The reason is that it was also necessary to consider the groundwater concentration of the selected compounds.

There was no doubt about selection of barbital from the barbiturates group - it has the lowest K_{ow} and K_{oc} (as mentioned above K_H is neglected) and it was found in high concentrations. Then there was a question between secobarbital, pentobarbital, and amobarbital; they all have high K_{ow} (not high in general but high in relation to this barbiturates group) and large respective medium - secobarbital - mobility. From these three compounds amobarbital was found in the highest concentration (see the Table 8.4) - therefore it was selected as the representative compound of the barbiturate group.

Concerning to sulfonamides group no doubt about sulfanilic acid selection - it has the lowest K_{ow} and K_{oc} from this group and is found in really high concentrations. Then sulfamethazine was selected - in relation to the sulfonamides group it has high K_{ow} value and was found in quite high concentration. As the third sulfonamides representative compound sulfaguanidine was selected - the K_{ow} and K_{oc} values are in between the already selected compounds and it was found in high concentration.

From the BTEX group only ethylbenzene was left out; it is similar to toluene but toluene was found in higher concentrations. Concerning to xylenes all of them can be modeled as one group (the RISC 4 software allows this possibility). The concentration set to the model is then the highest of the measured xylenes.

All chlorinated compounds are modeled except 1,1-DCE and trans-1,2-DCE. The reason why to leave out these compounds is following. 1,1-DCE was not found in any sample so it is obvious that it is not reasonable to model it. It was decided to model only one of cis-1,2-DCE and trans-1,2-DCE because they are very similar. Cis-1,2-DCE was chosen because it was found in higher concentrations.

9.3 RISC 4 Models Selection

The analytical phase (the risk assessment modeling) was done using the RISC 4 software. For the risk assessment modeling two different models were chosen - dissolved phase model (which is used when contaminants are already spread in groundwater) and vadose zone model (for modeling of contaminant transport from unsaturated zone to saturated zone). More information about the models is available in the Capture 4. Two endpoints (ecosystems potentially at risk) were modeled - the lake and the river. For these four cases two scenarios were modeled - one conservative without considering of compounds degradation and one with degradation of compounds considered. Simulation time was set to 100 years.

Dissolved phase model and vadose phase model were run for five different distances downgradient from the landfill to show how the concentrations of contaminants are decreasing with the distance. The tested points are 500 m, 1000 m, 1500 m, 2000m (distance of the river from the landfill), and 2250 m (distance of the lake from the landfill) far from the landfill.

At the endpoints - the river and the lake - two different scenarios were modeled - whole volume of river/lake mixing and 10% of river/lake mixing were modeled.

Together 28 models were run. All the data necessary as an input into RISC 4 program for modeling are shown in the Capture 9.4. The RISC 4 program generates its inputs and outputs summary.

9.4 The Input Data for the Modeling

There is necessary to input data about chemicals, source of contamination, unsaturated zone, aquifer, and surface water recipients - the river or the lake (the Table 4.1 summaries the input data needed for RISC 4 modeling). Following tables show values of all parameters which were entered into RISC 4 program to model dissolved source model and vadose source model and two endpoints - the river and the lake - for selected chemicals.

Table 9.2 - Chemicals input parameters

Chemicals	Molecular weight [g/mol]	Vapour pressure [mm Hg]	Solubility [mg/L]	K_H [-]	log K_{ow} [-]	K_{oc} [L/kg]	Degradation rate [d^{-1}]
Barbital	184.2	$1.59\cdot10^{-10}$	7 460	$1.47\cdot10^{-11}$	0.65	20.1	$4.7\cdot10^{-3}$
Amobarbital	226.28	$2.17\cdot10^{-11}$	603	$3.45\cdot10^{-11}$	2.07	106	$4.7\cdot10^{-3}$
Sulfamethazine	278	$8.62\cdot10^{-9}$	1 500	$7.88\cdot10^{-9}$	0.89	496	0
Sulfanilic acid	173	$2.02\cdot10^{-7}$	10 800	$3.64\cdot10^{-11}$	-2.16	10	0
Sulfaguanidine	214.25	$1.47\cdot10^{-7}$	2 200	$4.13\cdot10^{-14}$	-1.22	129	0
Benzene	78	95	1 750	0.228	2.1	59	$9.6\cdot10^{-4}$
Cis-1,2-DCE	96.9	200	3 500	0.167	1.9	36	$4.0\cdot10^{-2}$
PCE	165.8	19	200	0.754	2.7	160	$9.6\cdot10^{-4}$
Toluene	92.1	28	526	0.272	2.8	180	$2.5\cdot10^{-2}$
TCE	131.4	69	1 100	0.422	2.7	170	$4.0\cdot10^{-4}$
Vinyl chloride	62.5	3 000	2 760	1.11	1.5	19	$2.4\cdot10^{-2}$
Xylenes	106.2	8.8	198	0.29	3.3	240	$1.9\cdot10^{-3}$

Table 9.3 - Source input parameters

Source input parameters			
Dissolved model		Vadose model	
Source geometry [m]		Source geometry [m]	
Thickness	5	Thickness	5
Length (in the direction of GW* flow)	160	Length (in the direction of GW* flow)	160
Width (perpendicular to GW* flow)	150	Width (perpendicular to GW* flow)	150
		Depth to top of contamination	0.5
Source concentration [µg/L]		Source concentration [µg/L]	
Barbital	98.7	Barbital	563
Amobarbital	243	Amobarbital	651
Sulfamethazine	2 050	Sulfamethazine	2 400
Sulfanilic acid	28 000	Sulfanilic acid	35
Sulfaguanidine	6 580	Sulfaguanidine	94
Benzene	151	Benzene	-
Cis-1,2-DCE	2 200	Cis-1,2-DCE	50
PCE	4.97	PCE	37
Toluene	330	Toluene	-
TCE	27.52	TCE	290
Vinyl Chloride	121	Vinyl Chloride	340
Xylenes	65.73	Xylenes	-

*GW - groundwater

Table 9.4 - Unsaturated zone input parameters

Unsaturated zone input parameters	
Infiltration rate [cm/year]	40
Thickness of vadose zone [m]	1
Total porosity [-]	0.67
Residual water content [-]	0.66
Saturated conductivity [m/day]	0.038
Value of Van Genuchtens [-]	1.09
Fraction of organic carbon [g oc/g soil]	0.001
Soil bulk density [g/cm^3]	1.7

Table 9.5 - Aquifer input parameters

Aquifer input parameters	
Hydraulic gradient [-]	0.0012
Effective porosity [-]	0.33
Fraction of organic carbon [g oc/g soil]	0.005
Hydraulic conductivity [m/day]	4.6
Soil bulk density [g/cm^3]	1.7

Table 9.6 - Surface water recipients input parameters

Surface water recipients input parameters			
Lake		River	
Distance to SW edge [m]	2 250	Distance to SW edge [m]	2 000
Hydraulic conductivity of SW* bed [m/day]	10	Hydraulic conductivity of SW* bed [m/day]	10
Thickness of aquifer entering SW* [m]	10	Thickness of aquifer entering SW* [m]	10
Hydraulic gradient between GW* and SW* [-]	0.0012	Hydraulic gradient between GW* and SW* [-]	0.0012
Surface water flow rate [m^3/day]	194 100	Surface water flow rate [m^3/day]	153 684
Volume of lake [m^3]	465 000	Cross-sectional area [m^2]	11
Fraction of lake volume for mixing [-]	1	Fraction of cross-sectional area for mixing [-]	1
Fraction of organic carbon in sediment [g oc/g soil]	0.01	Fraction of organic carbon in sediment [g oc/g soil]	0.01

*GW – groundwater

*SW - surface water

9.5 Modeled Results and RCR

9.5.1 Groundwater Concentrations

There were modeled five different distances from the landfill in the direction of the groundwater flow (northwesterly) - 500 m, 1000 m, 1500 m, 2000 m, and 2250 m. Two models were used - dissolved phase model and vadose model. The groundwater concentrations which were modeled are shown in following tables. Firstly no degradation of compounds is considered and secondly degradation of compounds was modeled.

Dissolved Phase Model

Table 9.7 - Maximum modeled GW concentrations [μg/L]; dissolved phase model; no degradation

Chemicals	Distance from the landfill										GW quality criteria [μg/L]
	500 m		1000 m		1500 m		2000 m		2250 m		
	GW conc. [μg/L]	Occurred in year	GW conc. [μg/L]	Occurred in year	GW conc. [μg/L]	Occurred in year	GW conc. [μg/L]	Occurred in year	GW conc. [μg/L]	Occurred in year	
Barbital	11.9	71.1	5.04	98.8	2.99	100	2.07	100	1.78	100	ND*
Amobarbital	29.3	69.6	12.4	100	7.34	100	4.98	100	4.15	100	ND*
Sulfamethazine	246	100	91.3	100	28.8	100	5.32	100	1.81	100	ND*
Sulfanilic acid	3480	62.1	1480	95.2	875	100	605	100	521	100	ND*
Sulfaguanidine	794	94.6	336	100	198	100	132	100	108	100	ND*
Benzene	**18.2**	81.1	**7.73**	99.9	**4.58**	100	**3.15**	100	**2.7**	100	1
Cis-1,2-DCE	**265**	69.5	**112**	99.8	**66.5**	100	**45.9**	100	**39.5**	100	1
PCE	$6.00 \cdot 10^{-1}$	99.1	$2.54 \cdot 10^{-1}$	100	$1.49 \cdot 10^{-1}$	100	$9.53 \cdot 10^{-2}$	100	$7.48 \cdot 10^{-2}$	100	1
Toluene	**39.6**	99.3	**16.9**	100	**9.81**	100	**6.07**	100	4.61	100	5
TCE	**3.32**	99.8	**1.41**	100	$8.21 \cdot 10^{-1}$	100	$5.17 \cdot 10^{-1}$	100	$3.99 \cdot 10^{-1}$	100	1
Vinyl chloride	**14.5**	63	**6.16**	98.7	**3.65**	100	**2.52**	100	**2.18**	100	0.2
Xylenes	**7.93**	100	3.35	100	1.87	100	$9.98 \cdot 10^{-1}$	100	$6.72 \cdot 10^{-1}$	100	5

*ND not deffined

The concentrations of contaminants those limits are not met are highlighted by bold letters

Table 9.8 - Maximum modeled GW concentrations [µg/L]; dissolved phase model; degradation

Chemicals	Distance from the landfill										GW quality criteria [µg/L]
	500 m		1000 m		1500 m		2000 m		2250 m		
	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	
Barbital	$2.3\cdot10^{-4}$	17.2	$7.5\cdot10^{-8}$	20.9	$4.69\cdot10^{-11}$	25.1	$4.0\cdot10^{-14}$	28.5	$1.25\cdot10^{-15}$	31.9	ND*
Amobarbital	$5.67\cdot10^{-4}$	22.2	$1.65\cdot10^{-7}$	29	$1.16\cdot10^{-10}$	37	$9.84\cdot10^{-14}$	42.3	$3.08\cdot10^{-15}$	42.8	ND*
Sulfamethazine	246	100	91.3	100	28.8	100	5.32	100	1.8	100	ND*
Sulfanilic acid	3480	62.1	1480	95.2	875	100	605	100	521	100	ND*
Sulfaguanidine	794	94.6	336	100	198	100	132	100	108	100	ND*
Benzene	$7.26\cdot10^{-1}$	43.6	$2.69\cdot10^{-2}$	61.4	$1.72\cdot10^{-3}$	73.3	$1.25\cdot10^{-4}$	83	$3.5\cdot10^{-5}$	86.4	1
Cis-1,2-DCE	$1.25\cdot10^{-15}$	4.2	0	-	0	-	0	-	0	-	1
PCE	$2.39\cdot10^{-2}$	64.7	$9.5\cdot10^{-4}$	62.4	$5.67\cdot10^{-5}$	99.7	$4.1\cdot10^{-6}$	100	$1.15\cdot10^{-6}$	100	1
Toluene	$1.97\cdot10^{-12}$	8.9	0	-	0	-	0	-	0	-	5
TCE	$7.49\cdot10^{-1}$	86.3	$9.98\cdot10^{-2}$	100	$1.9\cdot10^{-2}$	100	$4.26\cdot10^{-3}$	100	$2.09\cdot10^{-3}$	100	1
Vinyl chloride	**5.77**	60	**1.17**	77.4	**$3.35\cdot10^{-1}$**	97.2	$1.12\cdot10^{-1}$	100	$6.75\cdot10^{-2}$	100	0.2
Xylenes	$2.91\cdot10^{-2}$	55.4	$2.46\cdot10^{-4}$	74.7	$3.36\cdot10^{-6}$	65	$5.77\cdot10^{-8}$	98.8	$7.96\cdot10^{-9}$	99.8	5

*ND not deffined

The concentrations of contaminants those limits are not met are highlighted by bold letters

As supposed with increasing distances from the landfill the contaminant concentrations are decreasing. According to the available groundwater quality criteria it is possible to say that in the distance of 500 m far from the landfill only criterion for PCE is met if no degradation occur. If degradation is considered only criterion for vinyl chloride is not met; the others contaminant concentrations are below (cis-1,2-DCE and toluene far below) the groundwater quality criteria.

In the distance of 1000 m groundwater quality criteria for PCE are met and also xylenes criteria are met if no degradation occurs. If degradation is taken into account all available groundwater quality criteria are met except of vinyl chloride where the concentration is around five times higher than the quality criterion. On the other hand the concentration of cis-1,2-DCE is modeled as zero; no cis-1,2-DCE should be found in this distance and farer.

In the distance of 1500 m groundwater quality criteria are met for PCE, xylenes, and also for TCE if no degradation is considered. If degradation is considered the concentration of vinyl chloride is still a little bit higher than the quality criterion. No concentration of cis-1,2-DCE and toluene are modeled in this distance if degradation is considered.

In the distance of 2000 m (it means the distance of the river) and no degradation considered the met criteria are for PCE, xylenes, and TCE - it means the same as in the distance of 1500 m but naturally the modeled concentrations are lower. Anyway the others groundwater quality criteria are still not met. If degradation is considered all groundwater quality criteria are met and cis-1,2-DCE and toluene concentration are modeled as zero.

In the distance of 2250 m (the distance of the lake) criteria for PCE, xylenes, TCE, and also for toluene are met if no degradation is considered. But concentration of benzene, cis-1,2-DCE, and vinyl chloride are still higher than groundwater quality criteria. If degradation is considered the situation is similar as in the distance of 2000 m - all groundwater quality criteria are met and cis-1,2-DCE and toluene concentrations are zero.

There exist no quality criteria for pharmaceutical compounds; it was decided to calculate RCR to assess the risk for the environment. The RCR was calculated also for BTEX and chlorinated compounds to see if the RCR assessment match the groundwater quality criteria. LC50 respective PNEC values were used the same as for groundwater samples RCR calculations. The used LC50 and PNEC values are shown in the Table 8.3 and in the

Table 8.5. Calculated RCRs for all distances from the landfill are shown in the Table 9.9 and in the Table 9.10.

Table 9.9 - RCRs for calculated concentrations of chemicals without degradation

Chemicals	Distance from the landfill					Potential of effect
	500 m	1000 m	1500 m	2000 m	2250 m	
Barbital	0.0102	0.0043	0.0026	0.0018	0.0015	no
Amobarbital	0.2382	0.1008	0.0597	0.0405	0.0337	no
Sulfamethazine	**59.5642**	**22.1065**	**6.9734**	**1.2881**	0.4383	**D***
Sulfanilic acid	**23.0464**	**9.8013**	**5.7947**	**4.0066**	**3.4503**	**yes**
Sulfaguanidine	**79.7910**	**33.7655**	**19.8975**	**13.2650**	**10.8532**	**yes**
Benzene	0.9100	0.3865	0.2290	0.1575	0.1350	no
Cis-1,2-DCE	**127.4038**	**53.8462**	**31.9712**	**22.0673**	**18.9904**	**yes**
PCE	0.1200	0.0508	0.0298	0.0191	0.0150	no
Toluene	**9.2093**	**3.9302**	**2.2814**	**1.4116**	**1.0721**	**yes**
TCE	**1.6600**	0.7050	0.4105	0.2585	0.1995	**D***
Vinyl chloride	**6.2500**	**2.6552**	**1.5733**	**1.0862**	0.9397	**D***
Xylenes	**6.1000**	**2.5769**	**1.4385**	0.7677	0.5169	**D***

*D potential of adverse effects differ with the distance

The concentrations of contaminants which present potential adverse effect are highlighted by bold letters

Table 9.10 - RCRs for calculated concentrations of chemicals with degradation

Chemicals	Distance from the landfill					Potential of effect
	500 m	1000 m	1500 m	2000 m	2250 m	
Barbital	$1.98\cdot10^{-7}$	$6.45\cdot10^{-11}$	$4.04\cdot10^{-14}$	$3.44\cdot10^{-17}$	$1.08\cdot10^{-18}$	no
Amobarbital	$4.61\cdot10^{-6}$	$1.34\cdot10^{-9}$	$9.43\cdot10^{-13}$	$8\cdot10^{-16}$	$2.5\cdot10^{-17}$	no
Sulfamethazine	**59.5642**	**22.1065**	**6.9734**	**1.2881**	0.4358	**D***
Sulfanilic acid	**23.0464**	**9.8013**	**5.7947**	**4.0066**	**3.4503**	**yes**
Sulfaguanidine	**79.7910**	**33.7655**	**19.8975**	**13.2650**	**10.8532**	**yes**
Benzene	0.0363	0.0013	0.0001	$6.25\cdot10^{-6}$	$1.75\cdot10^{-6}$	no
Cis-1,2-DCE	$6.01\cdot10^{-16}$	0	0	0	0	no
PCE	0.0048	0.0002	$1.13\cdot10^{-5}$	$8.2\cdot10^{-7}$	$2.3\cdot10^{-7}$	no
Toluene	$4.58\cdot10^{-13}$	0	0	0	0	no
TCE	0.3745	0.0499	0.0095	0.0021	0.0010	no
Vinyl chloride	**2.4871**	0.5043	0.1444	0.0483	0.0291	**D***
Xylenes	0.0224	0.0002	$2.58\cdot10^{-6}$	$4.44\cdot10^{-8}$	$6.12\cdot10^{-9}$	no

*D potential of adverse effects differ with the distance

The concentrations of contaminants which present potential adverse effect are highlighted by bold letters

The calculated RCRs show that selected barbiturates - barbital and amobarbital - do not pose treat for the environment in any case. If no degradation is considered the RCRs are in all cases lower than one; if degradation is considered the RCRs are in all cases far below one (in range of 10^{-6} to 10^{-18}).

On the other hand all modeled sulfonamides pose treat for the environment in all distances from the landfill; except sulfamethazine in the farthest modeled distance of 2250 m where the RCR ratio is 0.4. There are no differences for sulfonamides if degradation is considered or not because the degradation rate is set as zero - they are considered to be persistent in the environment. The calculated RCRs are quite high (the highest is 79.79 for sulfaguanidine) so concentrations of sulfonamides modeled in groundwater definitely present a danger for the environment.

RCRs for BTEX and chlorinated compounds were calculated to compare the danger for the environment according to the calculated ratios and according to the groundwater quality criteria. According to RCRs benzene and PCE do not pose treat in any distance in both cases - no degradation and degradation considered. On the other hand cis-1,2-DCE and toluene present a danger for the environment in all distances from the landfill if no degradation is considered. If no degradation is considered TCE, vinyl chloride, and xylenes pose risk only closer to the landfill, TCE in distance of 500 m, vinyl chloride in the distance of 2000 m, and xylenes in the distance of 1500 m.

If degradation is considered the situation changes completely because some of the degradation rate constant are quite high. If degradation is considered only vinyl chloride pose treat for the environment in the closest modeled distance of 500 m. Other RCRs for other BTEX and chlorinated compounds are below one; in some cases far below one especially in cases of cis-1,2-DCE and toluene.

Vadose Phase Model

Table 9.11 - Maximum modeled GW concentrations [µg/L]; vadose phase model; no degradation

Chemicals	Distance from the landfill										GW quality criteria [µg/L]
	500 m		1000 m		1500 m		2000 m		2250 m		
	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	
Barbital	11.7	100	$5.96\cdot10^{-2}$	100	$1.68\cdot10^{-5}$	100	$3.39\cdot10^{-10}$	100	0	-	ND*
Amobarbital	$2.5\cdot10^{-2}$	100	$2.35\cdot10^{-9}$	100	0	-	0	-	0	-	ND*
Sulfamethazine	0	-	0	-	0	-	0	-	0	-	ND*
Sulfanilic acid	1.19	100	$2.46\cdot10^{-2}$	100	$4.06\cdot10^{-5}$	100	$7.25\cdot10^{-9}$	100	$4.35\cdot10^{-11}$	100	ND*
Sulfaguanidine	$6.02\cdot10^{-4}$	100	$2.79\cdot10^{-12}$	100	0	-	0	-	0	-	ND*
Cis-1,2-DCE	$3.65\cdot10^{-1}$	100	$2.28\cdot10^{-4}$	100	$4.18\cdot10^{-9}$	100	0	-	0	-	1
PCE	$2.07\cdot10^{-5}$	100	0	-	0	-	0	-	0	-	1
TCE	$7.44\cdot10^{-5}$	100	0	-	0	-	0	-	0	-	1
Vinyl chloride	**7.48**	100	$4.43\cdot10^{-2}$	100	$1.51\cdot10^{-5}$	100	$3.89\cdot10^{-10}$	100	0	-	0.2

*ND not deffined

The concentrations of contaminants those limits are not met are highlighted by bold letters

Table 9.12 - Maximum modeled GW concentrations [µg/L]; vadose phase model; degradation

Chemicals	Distance from the landfill										GW quality criteria [µg/L]
	500 m		1000 m		1500 m		2000 m		2250 m		
	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	GW conc. [µg/L]	Occurred in year	
Barbital	$1.19\cdot10^{-10}$	23	0	-	0	-	0	-	0	-	ND*
Amobarbital	$8.05\cdot10^{-11}$	53.7	0	-	0	-	0	-	0	-	ND*
Sulfamethazine	0	-	0	-	0	-	0	-	0	-	ND*
Sulfanilic acid	1.19	100	$2.46\cdot10^{-2}$	100	$4.06\cdot10^{-5}$	100	$7.25\cdot10^{-9}$	100	$4.35\cdot10^{-11}$	100	ND*
Sulfaguanidine	$6.02\cdot10^{-4}$	100	$2.79\cdot10^{-12}$	100	0	-	0	-	0	-	ND*
Cis-1,2-DCE	0	-	0	-	0	-	0	-	0	-	1
PCE	$4.34\cdot10^{-7}$	100	0	-	0	-	0	-	0	-	1
TCE	$1.67\cdot10^{-5}$	100	0	-	0	-	0	-	0	-	1
Vinyl chloride	$9.2\cdot10^{-2}$	79.9	$3.2\cdot10^{-4}$	100	$9.92\cdot10^{-8}$	100	$2.4\cdot10^{-12}$	100	0	-	0.2

*ND not deffined

If vadose zone model is used the contaminant concentration in selected distances are completely different. If available groundwater quality criteria are considered the only quality criterion which is not met is the criterion for vinyl chloride in the distance of 500 m far from the landfill when no degradation is considered. In all other cases - with or without degradation - the criteria are met.

Furthermore with increasing distances no concentrations of compounds are modeled. In case of no degradation is considered no sulfamethazine was found immediately in the distance of 500 m. In the distance of 1000 m no sulfamethazine, PCE, and TCE were modeled. In the distance of 1500 m the only modeled compounds are barbital, sulfanilic acid, cis-1,2-DCE, and vinyl chloride while in the distance of 2000 m only barbital, sulfanilic acid, and vinyl chloride were modeled. In the distance of 2250 m the only modeled compound is sulfanilic acid. If degradation of compounds is considered there are no sulfamethazine and cis-1,2-DCE modeled immediately in the distance of 500 m. In the distance of 1000 m the only modeled compounds are sulfanilic acid, sulfaguanidine, and vinyl chloride. In the distance of 1500 m and 2000 m the modeled compounds are sulfanilic acid and vinyl chloride and in the distance of 2250 m only vinyl chloride was modeled.

Again RCRs were calculated to assess the ecological risk. The calculated RCRs are shown in the Table 9.13 and the Table 9.14.

Table 9.13 - RCRs for calculated concentrations of chemicals with degradation

Chemicals	Distance from the landfill					Potential of effect
	500 m	1000 m	1500 m	2000 m	2250 m	
Barbital	0.0101	$5.13 \cdot 10^{-5}$	$1.44 \cdot 10^{-8}$	$2.92 \cdot 10^{-13}$	0	no
Amobarbital	0.0002	$1.91 \cdot 10^{-11}$	0	0	0	no
Sulfamethazine	0	0	0	0	0	no
Sulfanilic acid	0.0079	0.0002	$2.69 \cdot 10^{-7}$	$4.80 \cdot 10^{-11}$	$2.88 \cdot 10^{-13}$	no
Sulfaguanidine	$6.05 \cdot 10^{-5}$	$2.8 \cdot 10^{-13}$	0	0	0	no
Cis-1,2-DCE	0.1755	0.0001	$2.01 \cdot 10^{-9}$	0	0	no
PCE	$4.14 \cdot 10^{-6}$	0	0	0	0	no
TCE	0.0037	0	0	0	0	no
Vinyl chloride	**3.2241**	0.0191	$6.51 \cdot 10^{-6}$	$1.68 \cdot 10^{-10}$	0	**D***

*D potential of adverse effects differ with the distance

The concentrations of contaminants which present potential adverse effect are highlighted by bold letters

Table 9.14 - RCRs for calculated concentrations of chemicals with degradation

Chemicals	Distance from the landfill					Potential of effect
	500 m	1000 m	1500 m	2000 m	2250 m	
Barbital	$1.02 \cdot 10^{-13}$	0	0	0	0	no
Amobarbital	$6.54 \cdot 10^{-13}$	0	0	0	0	no
Sulfamethazine	0	0	0	0	0	no
Sulfanilic acid	0.0079	0.0002	$2.69 \cdot 10^{-7}$	$4.8 \cdot 10^{-11}$	$2.88 \cdot 10^{-13}$	no
Sulfaguanidine	$6.05 \cdot 10^{-5}$	$2.8 \cdot 10^{-13}$	0	0	0	no
Cis-1,2-DCE	0	0	0	0	0	no
PCE	$8.68 \cdot 10^{-8}$	0	0	0	0	no
TCE	$8.35 \cdot 10^{-6}$	0	0	0	0	no
Vinyl chloride	0.0397	0.0001	$4.28 \cdot 10^{-8}$	$1.03 \cdot 10^{-12}$	0	no

As it is seen from the tables the only RCR which is higher than one is vinyl chloride ratio in the distance of 500 m from the landfill if no degradation is considered. This is the only danger for the environment if vadose zone model is used for calculations. All the others RCRs are lower than one which means that there is no danger for the environment.

9.5.2 Surface Water Concentrations

There were modeled two surface water recipients - river and lake. The river is about 2000 m north form the landfill; the lake is about 2250 m northwesterly from the landfill. It means there are two surface water recipients modeled in the direction of groundwater flow. There are two scenarios modeled - whole volume of the river or the lake is mixed with the polluted groundwater and 10% of the river or the lake is mixed with polluted groundwater.

River

Table 9.15 - Maximum modeled SW - the river - concentration; dissolved phase model; whole volume mixing

Chemicals	No degradation		Degradation		SW quality criteria [µg/L]
	Max. SW modelled conc. [µg/L]	Occurred in year	Max. SW modelled conc. [µg/L]	Occurred in year	
Barbital	$2.3\cdot10^{-3}$	100	0	-	ND
Amobarbital	$5.55\cdot10^{-3}$	100	0	-	ND
Sulfamethazine	$5.94\cdot10^{-3}$	100	$5.94\cdot10^{-3}$	100	ND
Sulfanilic acid	$6.75\cdot10^{-1}$	100	$6.75\cdot10^{-1}$	100	ND
Sulfaguanidine	$1.47\cdot10^{-1}$	100	$1.47\cdot10^{-1}$	100	ND
Benzene	$3.25\cdot10^{-3}$	100	$1.39\cdot10^{-7}$	83	30[A]; 230[B]; 370[C]
Cis-1,2-DCE	$5.12\cdot10^{-2}$	100	0	-	610[A]
PCE	$1.06\cdot10^{-4}$	100	0	-	ND
Toluene	$6.77\cdot10^{-3}$	100	0	-	50[A]; 170[B]
TCE	$5.77\cdot10^{-4}$	100	$4.75\cdot10^{-6}$	100	10[A,D]
Vinyl chloride	$2.82\cdot10^{-3}$	100	$1.25\cdot10^{-4}$	100	100[A]
Xylenes	$1.11\cdot10^{-3}$	100	0	-	30[A]; 61[B]

ND not defined, [A] UK EQS (United Kingdom), [B] ANZECC (Australia, New Zealand), [C] CCREM (Canada),
[D] EC WQO (European Commission)

Table 9.16 - Maximum modeled SW - the river - concentration; dissolved phase model; 10% of volume mixing

Chemicals	No degradation		Degradation		SW quality criteria [µg/L]
	Max. SW modelled conc. [µg/L]	Occurred in year	Max. SW modelled conc. [µg/L]	Occurred in year	
Barbital	$2.28\cdot10^{-2}$	100	0	-	ND
Amobarbital	$5.50\cdot10^{-2}$	100	0	-	ND
Sulfamethazine	$5.88\cdot10^{-2}$	100	$5.88\cdot10^{-2}$	100	ND
Sulfanilic acid	6.68	100	6.68	100	ND
Sulfaguanidine	1.46	100	1.46	100	ND
Benzene	$3.48\cdot10^{-2}$	100	$1.37\cdot10^{-6}$	83	30[A]; 230[B]; 370[C]
Cis-1,2-DCE	$5.02\cdot10^{-1}$	100	0	-	610[A]
PCE	$1.05\cdot10^{-3}$	100	0	-	ND
Toluene	$6.7\cdot10^{-2}$	100	0	-	50[A]; 170[B]
TCE	$5.71\cdot10^{-3}$	100	$4.7\cdot10^{-5}$	100	10[A,D]
Vinyl chloride	$2.79\cdot10^{-2}$	100	$1.24\cdot10^{-3}$	100	100[A]
Xylenes	$1.1\cdot10^{-2}$	100	0	-	30[A]; 61[B]

ND not defined, [A] UK EQS (United Kingdom), [B] ANZECC (Australia, New Zealand), [C] CCREM (Canada),
[D] EC WQO (European Commission)

As the above tables show all available surface water quality criteria are met in all cases. Even if the most conservative approach is used - it means 10% of mixing surface water and no degradation considered - the modeled concentrations are still far lower than the selected criteria.

RCRs were also calculated especially because of the compounds where no quality criteria are set.

Table 9.17 - RCRs for SW - the river - modeled concentrations; dissolved phase model

Chemicals	RCRs [-]				Potential of effects
	No degradation		Degradation		
	Whole volume mixing	10% volume mixing	Whole volume mixing	10% volume mixing	
Barbital	1.98E-06	1.96E-05	0	0	no
Amobarbital	4.51E-05	0.000447	0	0	no
Sulfamethazine	1.44E-03	0.014237	0.001438	0.014237	no
Sulfanilic acid	4.47E-03	0.044238	0.00447	0.044238	no
Sulfaguanidine	1.48E-02	0.146719	0.014772	0.146719	no
Benzene	1.63E-04	0.00174	6.95E-09	6.85E-08	no
Cis-1,2-DCE	2.46E-02	0.241346	0	0	no
PCE	2.12E-05	0.00021	0	0	no
Toluene	1.57E-03	0.015581	0	0	no
TCE	2.89E-04	0.002855	2.38E-06	2.35E-05	no
Vinyl chloride	1.22E-03	0.012026	5.39E-05	0.000534	no
Xylenes	8.54E-04	0.008462	0	0	no

All RCRs are lower than one. It means that there is no danger of adverse effect for the surface water respective the river.

If vadose phase model was used no surface water concentrations of selected chemicals were modeled (no tables with the results were created).

Lake

Table 9.18 - Maximum modeled SW – the lake - concentration; dissolved phase model; whole volume mixing

Chemicals	No degradation		Degradation		SW quality criteria [µg/L]
	Max. SW modelled conc. [µg/L]	Occurred in year	Max. SW modelled conc. [µg/L]	Occurred in year	
Barbital	$1.65\cdot10^{-3}$	100	0	-	ND
Amobarbital	$3.85\cdot10^{-3}$	100	0	-	ND
Sulfamethazine	$1.67\cdot10^{-3}$	100	$1.67\cdot10^{-3}$	100	ND
Sulfanilic acid	$4.83\cdot10^{-1}$	100	$4.83\cdot10^{-1}$	100	ND
Sulfaguanidine	$9.99\cdot10^{-2}$	100	$9.99\cdot10^{-2}$	100	ND
Benzene	$2.5\cdot10^{-3}$	100	0	-	30[A]; 230[B]; 370[C]
Cis-1,2-DCE	$3.66\cdot10^{-2}$	100	0	-	610[A]
PCE	$6.93\cdot10^{-5}$	100	0	-	ND
Toluene	$4.27\cdot10^{-3}$	100	0	-	50[A]; 170[B]
TCE	$3.7\cdot10^{-4}$	100	$1.93\cdot10^{-6}$	100	10[A,D]
Vinyl chloride	$2.02\cdot10^{-3}$	100	$6.26\cdot10^{-5}$	100	100[A]
Xylenes	$6.23\cdot10^{-4}$	100	0	-	30[A]; 61[B]

ND not defined, [A] UK EQS (United Kingdom), [B] ANZECC (Australia, New Zealand), [C] CCREM (Canada), [D] EC WQO (European Commission)

Table 9.19 - Maximum modeled SW – the lake - concentration; dissolved phase model; 10% of volume mixing

Chemicals	No degradation		Degradation		SW quality criteria [µg/L]
	Max. SW modelled conc. [µg/L]	Occurred in year	Max. SW modelled conc. [µg/L]	Occurred in year	
Barbital	$1.63 \cdot 10^{-2}$	100	0	-	ND
Amobarbital	$3.82 \cdot 10^{-2}$	100	0	-	ND
Sulfamethazine	$1.66 \cdot 10^{-2}$	100	$1.66 \cdot 10^{-2}$	100	ND
Sulfanilic acid	4.79	100	4.79	100	ND
Sulfaguanidine	$9.91 \cdot 10^{-1}$	100	$9.91 \cdot 10^{-1}$	100	ND
Benzene	$2.48 \cdot 10^{-2}$	100	$3.21 \cdot 10^{-7}$	86.4	30^{A}; 230^{B}; 370^{C}
Cis-1,2-DCE	$3.63 \cdot 10^{-1}$	100	0	-	610^{A}
PCE	$6.87 \cdot 10^{-4}$	100	0	-	ND
Toluene	$4.24 \cdot 10^{-2}$	100	0	-	50^{A}; 170^{B}
TCE	$3.67 \cdot 10^{-3}$	100	$1.92 \cdot 10^{-5}$	100	$10^{A,D}$
Vinyl chloride	$2 \cdot 10^{-2}$	100	$6.2 \cdot 10^{-4}$	100	100^{A}
Xylenes	$6.18 \cdot 10^{-3}$	100	0	-	30^{A}; 61^{B}

ND not defined, ^{A} UK EQS (United Kingdom), ^{B} ANZECC (Australia, New Zealand), ^{C} CCREM (Canada),
^{D} EC WQO (European Commission)

If lake as surface water recipient was modeled the situation is similar to the river modeling. All available surface water quality criteria are met for all modeled scenarios. RCRs were again calculated; the results are shown in the Table 9.20.

Table 9.20 - RCRs for SW – the lake - modeled concentrations; dissolved phase model

Chemicals	RCRs [-]				Potential of effects
	No degradation		Degradation		
	Whole volume mixing	10% volume mixing	Whole volume mixing	10% volume mixing	
Barbital	1.42E-06	1.4E-05	0	0	no
Amobarbital	3.13E-05	0.000311	0	0	no
Sulfamethazine	4.04E-04	0.004019	0.000404	0.004019	no
Sulfanilic acid	3.20E-03	0.031722	0.003199	0.031722	no
Sulfaguanidine	1.00E-02	0.099588	0.010039	0.099588	no
Benzene	1.25E-04	0.00124	0	1.61E-08	no
Cis-1,2-DCE	1.76E-02	0.174519	0	0	no
PCE	1.39E-05	0.000137	0	0	no
Toluene	9.93E-04	0.00986	0	0	no
TCE	1.85E-04	0.001835	9.65E-07	9.6E-06	no
Vinyl chloride	8.71E-04	0.008621	2.7E-05	0.000267	no
Xylenes	4.79E-04	0.004754	0	0	no

All RCRs are lower than one - in some cases far lower than one - which means there is no risk of adverse effect for the lake.

If vadose phase model was used to model surface water – the lake - concentration no concentrations of compounds were modeled (no tables with the results were created).

10. RESULTS DISCUSSION

In Denmark groundwater is usually used as source of drinking water so the groundwater quality is really important. Therefore the quality criteria are really strict. For vinyl chloride it is possible to say that the measuring method is not sensitive enough; the criterion is 0.2µg/L and the detection limit is 1µg/L. Anyway there was found concentration of 600µg/L of vinyl chloride in the groundwater sample which is far higher than the criterion.

Unfortunately there exist no quality criteria in relation to ecological harmfulness. Groundwater is considered to be source of drinking water so all the criteria are related to human health. Concerning to the pharmaceutical compounds the situation regarding the quality standards is even worst. There exist no criteria or limit values for pharmaceutical compounds neither in groundwater nor in surface water. It was never considered that pharmaceutical compounds as drugs can end up as groundwater or surface water pollutants.

The RCRs were calculated to assess the ecological harmfulness especially of pharmaceutical compounds but also of BTEX and chlorinated compounds. The RCR is calculated on the basis of measured or modeled groundwater concentration (PEC) and so called Predicted No Effect Concentration (PNEC) which was set according to LC50 values of the compounds and assessment factor of 1000. The assessment factor of 1000 is used if only limited information from short-term tests is available. The assessment factor of 1000 is considered to be a conservative approach so the RCRs calculations are considered to be also conservative. Concerning to LC50 setting the lowest value of experimental or estimated data was chosen (it is the rule of the RCR calculation method). The problem with RCRs are that not for all the compounds the LC50 values were set experimentally; respective for all the pharmaceutical compounds only estimated data are available. The data used for RCRs calculations are estimated data from the EPI Suite (Estimation Programs Interface – developed by U.S. EPA) software which is using the Structure Activity Relationship approach. As this approach was tested in some cases the values match very well with the experimental values but in other cases they differ quite significantly. It could be said that in cases of estimated LC50 values (which mean all pharmaceutical compounds) the calculated RCRs could be misleading; especially in the cases when the RCR ratio is just around one (e.g. 1.05 for pentobarbital). In these cases the ecological adverse effects have to be considered very carefully. On the other hand the RCRs calculated on the basis of concentrations measured directly below the landfill are for the sulfonamides much higher than one (they are in ranges of hundreds except of dapsone which was found in very low concentration). So there is no doubt about the ecological harmfulness.

Concerning to the soil contaminant concentration assessment the situation is more complicated. Quality criteria exist only for chlorinated compounds (BTEX soil concentrations were not measured) and no criteria for barbiturates and sulfonamides. RCRs can not be calculated because it is related to the aquatic environment. If only comparison of quality criteria and measured concentration of chlorinated compounds in soil was done it was realized that all the soil quality criteria for the chlorinated compounds are met. It seem to be quite strange because dangerous concentration of these compounds are found in groundwater bellow the landfill and the chemicals concentration in the groundwater is due to leachate of the chemicals from the soil respective waste disposed there. The reason of this situation could be that the disposal of these chemicals started in 1962 and has finished in 1975. So it is 44 years ago when the disposal of chemical waste has started (and consequently leaching of chemicals into groundwater has started) and 31 years ago when it has been finished. Significant amount of contaminants are already leached into the groundwater and the soil concentration of contaminants is supposed to be decreasing. This is in all probability the reason why all the soil quality criteria are met but dangerous concentration of contaminants were found in the groundwater. On the other hand the soil quality criteria seem to be less strict than the groundwater quality criteria. But anyway the first theory is supported also by the RISC 4 modeling when the modeled concentrations of vadose phase model are much lower than the modeled concentrations of dissolved phase model (it is discussed more detailed below). As written above there exist no soil quality criteria for sulfonamides and barbiturates. It is possible only to assume that the situation is similar as for the chlorinated compounds. However there were modeled vadose phase model using RISC 4 program which models leaching of contaminants from the soil to the groundwater and calculates concentrations of the leached contaminants in the groundwater. This is a possibility how to assess the risk of contaminated soil. The results of these models are discussed below.

There were modeled two models - dissolved phase model and vadose phase model. The modeled concentrations of these two models differ significantly. The concentrations modeled by vadose phase model are much lower than these modeled by dissolved phase model. This big difference between the modeled concentrations support the theory described in previous paragraph (the significant part of contamination is already leached into the groundwater). In this case the dissolved phase model seems to give more realistic results. The used concentrations for modeling of contamination spreading are the real measured concentrations in the groundwater while the vadose zone model is using modeled concentrations which were calculated on the basis of leaching of contaminants from the soil. Every calculation models have limitations and are based on average or supposed values so directly measured concentrations are for sure more precise. Furthermore vadose zone model in fact combines vadose model and dissolved model - the vadose model models leaching of contaminants from the soil and calculate the concentrations of contaminants in groundwater which are then used as starting concentrations for dissolved phase model which models spreading of contaminants in subsurface (more information about the models is available in the Capture 4). All these reasons support the theory that dissolved phase model gives more realistic results.

Following discussion is concerned to the dissolved phase models because the vadose zone models results pose insignificant treat in comparison with the dissolved phase models results.

If strictly conservative approach is used for the groundwater concentrations modeling (no degradation of compounds is considered) there is significant risk of potential adverse effects. Of course the risk is higher in closer distances to the landfill. Anyway there is still significant risk in the farthest modeled distance. According to this model the landfill present serious danger for the groundwater below the landfill and in the direction of groundwater flow (which is found to be northwesterly to north according to seasonal variations) before it reach surface water recipients.

If not so conservative model is used (degradation of compounds is considered) the risk of adverse effects has decreased significantly. But there is the problem that sulfonamides are considered to be persistent (no degradation occur) so the same concentrations are modeled and the same RCRs are calculated for the both cases. This means that high concentrations are modeled or RCRs higher than one are calculated in all modeled distances from the landfill. If degradation is considered this persistent compounds present the biggest threat for the groundwater.

Concerned to the surface water recipients the situation looks positively - there were modeled no dangerous concentrations of contaminants neither in the river nor in the lake. All the RCRs are lower than one. It seems the mixing ratio is high enough to dilute the contaminants to no harmful level even if only 10% of the volumes are considered for the mixing.

It is necessary to keep in mind that all the RCRs calculations and subsequently the risk assessment follow the conservative approach. According to this conservative approach there were calculated RCRs far higher than one in cases of sulfonamides (respective sulfanilc acid and sulfaguanidine) which are considered to be persistent in the environment. This is one of the most dangerous features for the environment - these compounds do not degrade so they are spread through the environment unchanged. Another high treat discovered during the risk assessment poses vinyl chloride - it was modeled in dangerous concentration 500 m far from the landfill even if degradation was considered. The width of the plume in this distance was modeled to 530 m so it presents large area which is contaminated by dangerous concentration of the carcinogenic compound. The width of the plumes around the surface water recipients shores are 1430 m and 1500 m by the river and the lake respectively (it represents whole east shore of the lake).

During risk assessment was discovered that the groundwater in this area is really polluted and it is not recommended to use the groundwater for any purposes (neither for irrigation).

All the upper mentioned contamination is considered to the shallow aquifer but there is also a possibility of contamination of the deep aquifer. The contaminants are presented in the groundwater already long time so they may penetrate the 1 m thick clay/silt layer. In the previous investigation there was made one borehole trough the clay/silt layer which shows some contamination presented in the deep aquifer. More investigation of the deep aquifer was not done mainly because of two reasons - the boreholes through the clay/silt layer can damage the "impermeability" of the layer and the contaminants can enter the deep aquifer along the wells; second reason is high cost of this deep boreholes. Concerned to the contamination of the deep aquifer calculation models may be used to model possible permeability of the clay/silt layer. But this is beyond the scope of this project.

Another investigated item of this study is the pharmaceutical compounds environmental fate and behavior. These chemicals were developed as drugs so it was never considered that these compounds can end up in the environment and cause its pollution. Just a few studies have been done about environmental fate and transport of these pollutants. This survey has investigated their fate and behavior in the subsurface; it has been compared to the fate and the transport in human bodies.

Barbiturates absorb very rapidly to plasma protein and are not distributed widely to tissues. Similar environmental fate can be supposed. If the concentration of barbiturates in groundwater and soil are compared, the concentrations in soil are much higher. This support the theory that barbiturate tend to sorb and their mobility is low. But K_{oc} values indicate very large to medium mobility in soil with a low tendency to sorb onto soil particles. On the basis of these fact is difficult to generalize barbiturates environmental fate. The leaching tests showed that the soil samples have not been homogenous so the measured soil concentration may be misleading. On the other hand all the K_{oc} values are estimated values on the basis of the Structure Activity Relationship. So what is more relevant fact? RISC 4 modeling also does not give sufficient answer. It is a mathematical model so it calculates only according to the entered data. If K_{oc} values which indicate large mobility are entered the modeled situation will supports the large mobility of the compounds.

Sulfonamides are widely distributed to tissues and srob to plasma protein. It indicates large mobility in soil with small tendency to sorb onto soil particles. If comparison of contaminants' groundwater concentrations and soil concentrations is done, there are in some cases very similar (nearly the same) concentration found in the soil and the groundwater. Sometimes the soil concentrations are much lower than the groundwater concentrations. In two cases the concentration in the soil was higher than the concentration in the groundwater. The similar or higher concentrations in the groundwater and the soil support the theory that sulfonamides are mobile compounds with a small tendency to sorb. But what about the two compounds which have higher concentration in the soil? One of them is dapsone which has (according to K_{oc} value) low mobility in soil. The second one is sulfadoxine which is supposed to have large mobility in soil. This may support the fact that the soil samples were not homogenous and the measured soil concentrations may be misleading. Anyway sulfonamides K_{oc} values vary from very large to low mobility in soil. This fact also supports the theory that generally sulfonamides are rather mobile compounds with a small tendency to sorb.

On the basis of upper mentioned facts is difficult to give general assumption of barbiturates and sulfonamides behavior in subsurface.

11. CONCLUSION

The goal of the study was to test the RISC 4 software for the groundwater risk assessment. This testing was preceded by several substeps which become inherent part of this study and bring contribution to the risk assessment procedure in general.

Firstly information about the ecological risk assessment was gathered and a capture about how to conduct the ecological risk assessment was written. This is an important part of the project because information about the ecological risk assessment conduction is not easily accessible.

Secondly the special chemical data sheets were developed. These data sheets gathered chemicals' data which are necessary for the ecological risk assessment. All accessible information about chemicals of concern was gathered and if relevant to the ERA included into the data sheets. Some data are experimental and some data are estimated. The data included in the data sheets are information about dissociation, volatility, sorption, bioaccumulation, biodegradability, ecotoxicity, and about classification of the chemicals. The data sheets are available in the Appendix B.

Another substep necessary to overcome during the study was to find a methodology for representative compounds selection. There were too many chemicals presented in the samples; it was not possible to model all of them together by the RISC 4 software. It was necessary to develop a methodology for representative contaminants selection. Basically the selection criteria are to choose compounds with the highest and the lowest K_{ow}, (reflects the bioaccumulation ability of compounds), K_{oc} (reflects soil mobility of compounds), and K_H (reflects volatility from aqueous solutions) values; this has to be combined with the compounds concentrations found in the groundwater. This methodology can be followed in any other studies where representative compound selection needs to be done.

As written above the main focus of this study is to test the RISC 4 software for the groundwater risk assessment. The outcomes of the software testing are the main contribution of this project. The software was tested on the basis of the case study of the Grindsted landfill.

The software RISC 4 is presented as a tool for the ecological risks evaluation. According to my experience the RISC 4 can be successfully used for modeling of groundwater movement and contaminants movement and fate. But for a purpose of the groundwater risk assessment it has to be combined with another tool to assess the ecological risks. In fact the RISC 4 program is not supposed to be used for the groundwater risk assessment; only surface water can be chosen as an endpoint of the modeling. The groundwater is used only as a "transport mean" of contaminants threatening surface water. Also only surface water quality criteria are included in the program so only surface water modeled concentrations can be assessed by the program. But also the surface water quality criteria are missing for many compounds. Furthermore there was realized a problem when the modeled concentrations were compared with the surface water quality criteria. There are modeled surface water concentrations and these concentrations are reported in the program output file. But when these modeled concentrations are compared to the program available surface water quality criteria the program generates different concentrations of the contaminants. So users have to check really carefully all data (not only in this section) to avoid mistakes. This is a contributing factor why I suggest using of the software only for modeling of the groundwater concentrations and then using of other tool for the risk evaluation.

The software is able to model contaminants' groundwater concentrations in any distances from the source. Those modeled concentrations can be then compared with the groundwater standards if exists or use as PEC for RCRs calculations or other purposes. Modeling of contaminants transport and fate is difficult task so for this purpose the RISC 4 is really very helpful. If the RISC 4 is combined with proper risk evaluation tool it can be successfully used for modeling of contaminants concentrations in the subsurface.

Concerned to the surface water risk evaluation I find the situation similar. Even if the program was developed to assess risks for surface water the modeled surface water concentrations have to be compared to the surface water quality criteria or RCRs have to be calculated to assess the risk for the surface water. As written above the software generates mistakes during the surface water contaminant concentrations modeling and furthermore the surface water quality criteria are not available for many compounds so the user has to find the criteria himself anyway.

To conclude the RISC 4 software testing: during the study was realized that the RISC 4 software is possible to use as an inherent part of the risk assessment itself. The RISC 4 software is recommended to be used for modeling of groundwater pollutants concentrations in any distances from the source. The source pollution concentrations have to be known. It may be concentrations found in groundwater or in soil. The RISC 4 software has to be combined with a methodology for the risk evaluation. In this particular case the groundwater limits and Risk Characterization Ratio (RCR) was used.

Using of the RCR for the ERA respective the groundwater RA is another tested item of this study. RCR is known as a factor characterizing surface water risks; the LC50 or EC50 or NOEC of surface water organisms (fish, daphnia, and algae) are used for the RCR calculation. It has been tested in this study if is it possible to use the RCR also for the groundwater risk evaluation. It was realized that the RCR calculations correspond to the groundwater quality criteria. When the groundwater quality criteria were not met the RCR was higher than one (poses risk for the environment) and when the criteria were met the RCR was lower than one (does not pose risk for the environment). For vinyl chloride the RCR was even more conservative - the groundwater quality criterion was met but RCR was higher than one. This comparison shows that the RCR can be successfully used as a criterion also for groundwater. The RCR calculation can be therefore used if the groundwater quality criteria are missing.

This opens another discussion which parameter is better to use for the risk evaluation - the groundwater quality criteria or the RCR? For the purpose of the environmental risk assessment I would suggest the RCR calculation instead of simple using groundwater limits. The reasons are following: the groundwater quality criteria do not exists for all compounds and are related to human health adverse effects. But the purpose is to evaluate risk for the environment. Therefore using of the RCRs which are related to the environment is supposed to give more precise risk evaluation and can be calculated also for compounds where the quality criteria are missing.

After all the testing I would suggest for the groundwater risk assessment combination of the RISC 4 software (as a tool for groundwater concentrations modeling) and the RCR (as a risk evaluation quotient). The combination of these two methods seems to give reasonable risk assessment outcomes. The conservativeness of the methodology can be driven during the process by choosing of the models without or with degradation, respective low-end or high-end degradation rates.

During the modeling also the influence of the degradation to the contaminants movement was tested. It was found out that the degradation influences the contaminant spreading significantly. Thus proper degradation constant is very important parameter which influences the risk assessment very much. Unfortunately it is not easy to set proper degradation constant. The degradation rate of compounds is strongly dependent on surrounding conditions; the same compound can have different degradation constant in different areas. It is usually not possible to determine the degradation rate for the certain area so generally set degradation rates are used. Those rates may not be fully realistic. Anyway it is recommended to use estimated degradation rates than do not consider degradation of compounds that are supposed to undergo degradation. Without the degradation the risk assessment procedure becomes too conservative. If low-end degradation rates are used the modeling procedure is conservative enough and the results are more realistic then if no degradation of compounds is considered.

Another investigated item of this project is fate and transport of the pharmaceutical compounds (sulfonamides and barbiturates) in the environment respective in the subsurface. Sulfonamides and barbiturates were developed as drugs so environmental pollution by these compounds was not supposed. Therefore data necessary for environmental investigation of these chemicals is difficult to obtain. Now all the investigated compounds have its own data sheet that includes environmental data of tested sulfonamides and barbiturates. So this data are easily available for purposes of the environmental investigation.

Unfortunately the survey does not give sufficient answer to the question about the environmental fate and transport of sulfonamides and barbiturates. Not enough information to generalize their behavior was obtained (it is discussed in details in the Capture 10). On the basis of all obtained information I would support the theory that environmental behavior of these chemicals is similar to behavior in human bodies. It means that sulfonamides are mobile compounds with a small tendency to sorb onto soil particle while barbiturates tend to sorb and are not distributed in the subsurface so fast. But this is just an assumption. To prove or disprove the assumption experimental survey of the behavior in soil has to be done and experimental K_{oc} values measured.

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ABBREVIATIONS

ANZECC	Australian and New Zealand Environment Conservation Council
BCF	bioconcentration factor
BOD	biological oxygen demand
BTEX	benzene, toluene, ethylbenzene, xylenes
CCREM	Canadian Council of Ministers for the Environment Fresh Aquatic Life Guideline
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CNS	central nervous system
COD	chemical oxygen demand
COD	chemical oxygen demand
DCE	dichloroethylene
DNAPL	dense non-aqueous phase liquids
DOC	dissolved organic carbon
EC WQO	European Commission Water Quality Objectives
EC50	effective concentration where 50 % of tested population exhibit a response
EPI	Estimation Programs Interface
ERA	environmental risk assessment
f_{oc}	fraction of organic carbon [-]
GC/MS	gas chromatography/ mass spectrometry
K_d	distribution coefficient [l·kg-1]
K_H	Henry’s law coefficient [atm·m^3·mol^{-1}]
K_{oc}	organic carbon partition coefficient [l·kg-1]
K_{ow}	octanol-water partition coefficient [dimensionless, but truly l·l-1]
K_p	partition coefficient [l·kg-1]
L/S ratio	liquid/soil ratio
LC/MS/MS	liquid chromatography/ mass spectrometry/ mass spectrometry
LC50	lethal concentration that kills 50 % of tested polulation
LNAPL	light non-aqueous phase liquids
NAPL	non-aqueous phase liquids
NOAA	National Oceanic and Atmospheric Administration
NOEC	no observed effect concentration
NVOC	non volatile organic compounds
OTA	The Office of Technology and Assessment
PCE	tetrachloroethylene
PEC	predicted environmental concentration
PEL	probable effect level
PNEC	predicted no effect concentration
RA	risk assessment
RBCA	risk-based corrective action
RCR	risk characterization ratio
RISC 4	Risk - Integrated Software for Cleanups
TCE	trichloroethylene

TOC	total organic carbon
U.S. EPA	The United States Environmental Protection Agency
UET	upper effects threshold
UK EQS	United Kingdom Environmental Quality Standards
US AWQC	United States Ambient Water Quality Criteria
VC	vinyl chloride
XOC	xenobiotic organic compound

APPENDIXES' CONTENTS