On the Use of Groundwater Contaminant Transport Modelling in Risk Assessments

Master’s Thesis in Applied Environmental Measurement Techniques

STEPHANIE DURIEZ

Department of Civil and Environmental Engineering
Division of GeoEngineering
Engineering Geology
CHALMERS UNIVERSITY OF TECHNOLOGY
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Master’s Thesis 2005:115
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Department of Civil and Environmental Engineering
Division of GeoEngineering
Engineering Geology
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone: + 46 (0)31-772 1000

Cover:
Lead transport modelling.

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ABSTRACT

Groundwater represents an important source of drinkable water, especially in Sweden where 50% of municipalities drinking water is supplied by groundwater. However, groundwater, as other water supplies, is more and more exposed to pollution which results in contamination of groundwater and soil that is in contact. Transport processes in subsurface water are the major pathways for contaminant spreading from contaminated areas to groundwater supplies, lakes or streams. Still, due to complex hydrogeological settings and to the high technical and scientific knowledge that are required, predictions of groundwater contaminant transport are rarely performed in risk assessments in Sweden. Nowadays, a number of commercial computer softwares have been developed and are available for advanced numerical modelling, capable of realistic handling of complex hydrogeological conditions. The main objective of this project was to set up a groundwater contaminant transport model for the Wockatz site, in eastern Göteborg, which exhibits a high contamination of soil and groundwater. Several groundwater flow and contaminant transport modellings have been carried out with Groundwater Modelling System (GMS) software, for the particular scenario where the upper layer of contaminated filling material would have been replaced by clean soil with more or less the same hydraulic characteristics. As the thesis work went along, many improvements were carried out of the models in order to make them as accurate and realistic as possible. Those models have allowed to get a quite good knowledge of the contaminant transport conditions at the Wockatz site, even if they only correspond to particular scenario, and the contaminant discharge to the adjacent river could be estimated. Moreover, a short evaluation of GMS as a tool for advanced numerical modelling of groundwater contaminant transport in risk assessments was made.

Key words: modelling, groundwater, flow, contaminant transport
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Acknowledgements

I would like to warmly thank my supervisor, Ph.D. Lars Rosén at the Department of GeoEngineering at Chalmers University of Technology, for the time he had devoted to me and for the confidence he had put in me, for his numerous sensible advises, for his endless source of help and support, for helping me to understand difficult points and for making sure my project went on well. I also would like to thank Pär-Erik Back, Ph.D. candidate at the department of GeoEngineering at Chalmers University of Technology, for his wise comments and his pertinent suggestions.

Finally, I would like to thank my friends and my family for support and encouragement.

Göteborg, November, 2005

Stéphanie Duriez
Notations

$A$ Variable notation for cross sectional area
$B_d$ Variable notation for bulk density
$C$ Variable notation for solute concentration
$C^*$ Variable notation for amount of sorbed solute
$D_e$ Variable notation for diffusion coefficient
$D_L$ Variable notation for longitudinal hydrodynamic dispersion coefficient
$D_s$ Variable notation for soil moisture diffusion coefficient
$D_T$ Variable notation for transverse hydrodynamic dispersion coefficient
$D^*$ Variable notation for effective diffusion coefficient
$F$ Variable notation for mass flux
$F_L$ Variable notation for linear mass flux
$J$ Variable notation for is the total flux of solute
$K$ Variable notation for hydraulic conductivity
$K_f$ Variable notation for partition coefficient
$K_s$ Variable notation for saturated hydraulic conductivity
$Q$ Variable notation for volumetric discharge of water
$S$ Variable notation for storage coefficient
$S_e$ Variable notation for effective saturation
$S_w$ Variable notation for saturation ratio
$T$ Variable notation for transmissivity
$V_m$ Variable notation for total volume of material
$V_p$ Variable notation for non-solid volume (pores and liquid)

$b$ Variable notation for saturated thickness
$k$ Variable notation for intrinsic permeability
$g$ Variable notation for gravitational constant
$h$ Variable notation for head
$h_b$ Variable notation for bubbling pressure
$n$ Variable notation for total porosity
$n_e$ Variable notation for effective porosity
$q$ Variable notation for convective soil moisture flux
$r_f$ Variable notation for retardation factor
$v$ Variable notation for darcy velocity
$v_x$ Variable notation for average linear velocity
$t$ Variable notation for time
$z$ Variable notation for depth below the surface
$dh/dl$ Variable notation for hydraulic head gradient
$\partial C/\partial x$ Variable notation for concentration gradient
$\partial C/\partial t$ Variable notation for change in concentration with time
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Variable Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_L$</td>
<td>Variable notation for longitudinal dynamic dispersivity</td>
</tr>
<tr>
<td>$\alpha_T$</td>
<td>Variable notation for transverse dynamic dispersivity</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Variable notation for experimentally derived parameter</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Variable notation for dynamic viscosity</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Variable notation for porosity</td>
</tr>
<tr>
<td>$\theta_a$</td>
<td>Variable notation for ratio of volume of air to total volume of the soil</td>
</tr>
<tr>
<td>$\theta_i$</td>
<td>Variable notation for irreducible minimum water content</td>
</tr>
<tr>
<td>$\theta_s$</td>
<td>Variable notation for volumetric water content at saturation</td>
</tr>
<tr>
<td>$\theta_w$</td>
<td>Variable notation for volumetric water content</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Variable notation for fluid density</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Variable notation for tortuosity coefficient</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Variable notation for tension or capillary suction</td>
</tr>
</tbody>
</table>
1 Introduction

Groundwater, under most conditions, is safer and more reliable for use than surface water. Part of the reason for this is that surface water is more readily exposed to pollutants from for example factories or traffic than groundwater. Thus, groundwater is an important source of drinking water in Sweden as well as in other countries. In Sweden, 50% of municipal drinking water is groundwater (Thunvik and Lindström, 2004). This by no means says that groundwater is invulnerable to contamination. It generally has a high quality standard in Sweden but today different kinds of human impacts are increasingly contaminating the groundwater resources. Any chemicals that are easily soluble and penetrate the soil are prime candidates for groundwater pollutants. Once it is contaminated, it is extremely difficult and costly to remove the contaminants from groundwater (Gurganus, 1993). Therefore, efforts are often put on protective measures instead. In order to know if, and to what extent groundwater is endangered, knowledge of the changes in groundwater quality is needed.

Contaminant transport in subsurface water is of paramount importance since it is the major pathway for contaminants transport from contaminated areas to various receptors such as groundwater supplies, lakes or streams. It encompasses physical, chemical and biological mechanisms which affect rates of migration, degradation and ultimate remediation. Therefore, in order to be able to remediate a contaminated site, it is necessary to understand and predict groundwater transport processes. Nevertheless, such predictions are rather complicated because of the often complex hydrogeological settings and of the high technical and scientific knowledge that are required. Thus, predictions of groundwater transport are rarely performed in risk assessment in Sweden. Nowadays, a number of commercial computer softwares have been developed, and numerical groundwater modelling appears to be one of the most efficient methods for groundwater transport predictions, capable of realistic handling of complex hydrogeological conditions. However, these methods have little application in Sweden and there is a need to apply and evaluate the applicability of these methods on Swedish conditions.

The main purpose of this thesis work was to set up a groundwater transport model for the Wockatz site, in eastern Göteborg. This site exhibits a high contamination of soil and groundwater and therefore represents a potential threat for the adjacent Göta älv river. The modelling was carried out with Groundwater Modelling System (GMS) software, which is one of the most sophisticated groundwater modelling tools available today, and which can provide, among other things, numerical modelling of groundwater flow and contaminant transport. The use of this software had two main objectives. The first one was obviously to gain increased knowledge of the contaminant transport conditions at the Wockatz site with special emphasis on the contaminant load on Göta älv. This is necessary in order to predict the contaminant spreading and to be able to remediate the site. But the purpose was also to evaluate the use of a commercial software for advanced numerical modelling of groundwater contaminant transport assessments at contaminated site. Indeed, it is interesting to know how this kind of software can be used by non-experts, i.e. by people having some hydrogeological knowledge but not specifically in numerical computer modelling.
2 Description of the studied area: the Wockatz site

2.1 Generalities

The project was carried out for Wockatz landfill site, which is located in the eastern part of Göteborg. The site exhibits conditions typical of the Göteborg area, such as extensive contamination of the soil and groundwater due to industrial activities. Wockatz scrap yard was in operation during period between 1930s and 1993, threatening to contaminate the Göta älv, located nearby and serving as a water supply for Göteborg (see Figure 2.1). The environmental quality of water has improved during the last 20 years and now has a high protection value, due to its so-called Natura 2000 classification. The high environmental protection value is also due to both the ecosystems in the river and in the river estuary. Maps of Sweden and of Göteborg, with the localisation of Wockatz site, can in found in Appendices A and B.

![Figure 2.1](image)

*Figure 2.1  Wockatz scrap yard, adjacent to the Göta älv.*

2.2 Geology

The scrap yard now represents a quite flat area. The stratigraphy of the site is filling material on top of glaciomarine clay (see Figure 2.2). The filling material is a mixture of grains of different sizes from clay to sand, gravel and boulders, including also different kind of anthropogenic materials like household scrap, construction materials, rubber, etc. The underlying layer of glaciomarine clay is a kind of soil that swells upon wetting and shrinks upon drying. Potential problems associated with this type of soil include land slippage and slope instability, shrinking and swelling of clay, poor foundation support, and poor drainage. Clay has a very low hydraulic conductivity and therefore could be considered as practically impermeable. Thus, the main groundwater flow occurs in the level of filling materials (Cao et al., 2004).
Figure 2.2  Stratigraphy of the site.

The thickness of filling material is roughly between 50 cm and 1 m. The aquifer of the studied area is unconfined, i.e. the water table is at atmospheric pressure, and thus it is able to rise and drop.

2.3 Dimensions and orientation

The site is approximately $150 \times 150$ m long and is oriented as shown Figure 2.3.

Figure 2.3  Wockatz site map.

Note: the thick pink line represents the boundaries of the field while the thick blue line represents the river boundary. The red dots represent the observation wells and/or the sampling spots.
2.4 Contamination

The Wockatz site is about to be adapted as residential land and therefore needs to be remediated to meet environmental standards for residential area. The site has already been investigated by a consulting company and by Chalmers, and it was discovered that the site is contaminated by metals and oil, with concentration values over the Environmental Protection Agency (EPA) guidelines in some parts of the site. Metal scrap was processed on the site and transported by rail or boat, leading to leakage and contamination of the soil. Old batteries, which used to be stored on the Wockatz site, is an obvious source of contamination of the site and subsequently of the river by lead. Table 2.1 gathers some contaminants concentration data that were obtained from a sampling campaign carried out by Chalmers in November 2004. In bracket is given the current conditions assessment according to the Swedish EPA.

<table>
<thead>
<tr>
<th>Location</th>
<th>Cadmium (µg/l)</th>
<th>Copper (µg/l)</th>
<th>Lead (µg/l)</th>
<th>Zinc (µg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well 0203</td>
<td>0.02 (very low)</td>
<td>1.45</td>
<td>5.40 (high)</td>
<td>551.86 (high)</td>
</tr>
<tr>
<td>Well 0204</td>
<td>2.79 (high)</td>
<td>13.82</td>
<td>0.07 (very low)</td>
<td>1683.41 (very high)</td>
</tr>
<tr>
<td>Well 0205</td>
<td>0.13 (moderate)</td>
<td>2.73</td>
<td>0.06 (very low)</td>
<td>79.13 (moderate)</td>
</tr>
<tr>
<td>Well 0206</td>
<td>0.01 (very low)</td>
<td>2.01</td>
<td>0.00 (very low)</td>
<td>12.68 (low)</td>
</tr>
<tr>
<td>Well 0208</td>
<td>0.63 (moderate)</td>
<td>32.87</td>
<td>3.02 (high)</td>
<td>90.07 (moderate)</td>
</tr>
<tr>
<td>Well 0209</td>
<td>0.40 (moderate)</td>
<td>16.14</td>
<td>0.33 (low)</td>
<td>75.11 (moderate)</td>
</tr>
<tr>
<td>Surface water 9804</td>
<td>0.09 (low)</td>
<td>4.15</td>
<td>0.12 (very low)</td>
<td>20.50 (moderate)</td>
</tr>
<tr>
<td>Surface water 9810</td>
<td>0.327 (moderate)</td>
<td>19.64</td>
<td>1.88 (moderate)</td>
<td>253.18 (moderate)</td>
</tr>
<tr>
<td>Surface water 9813</td>
<td>0.10 (moderate)</td>
<td>9.82</td>
<td>0.19 (very low)</td>
<td>40.50 (moderate)</td>
</tr>
</tbody>
</table>

Those values confirm that groundwater is quite contaminated. Nevertheless, the contamination is unevenly distributed, and some parts of the field are more sensitive than others. For those regions, current conditions have to be considered as serious risks.

For an effective remediation of the site, having a precise idea of the transport is helpful. Setting up a groundwater contaminant transport modelling from sampling data may thus be useful for the Wockatz site.
3 Groundwater contaminant transport

Groundwater contamination occurs when man-made products such as gasoline, oil, road salts and chemicals get into the groundwater and cause it to become unsafe and unfit for human use. Those contaminants undergo transport processes that contribute to spatial and temporal changes in concentrations. These processes tend to spread the contamination, but on the other hand they are also important for natural attenuation of plumes in aquifer systems. Some chemical processes can also occur, which can result in decreasing the mass of dissolved pollutants. Groundwater contaminant transport modelling is an interesting tool to use in order to predict the contamination distribution of a site.

3.1 Groundwater properties

Groundwater is characterised both by its vertical and its horizontal distribution. Vertically, groundwater is divided in two main parts: saturated and unsaturated (or vadose) zone. These two parts are generally separated by the water table. The horizontal distribution of subsurface water depends on several parameters that are characteristics from the porous medium and groundwater. These parameters determine the rate and the direction of groundwater flow.

3.1.1 Porosity

The porosity of a medium is the proportion of the non-solid volume to the total volume of material, and is defined by the ratio:

\[ \phi = \frac{V_p}{V_m} \]  

(3.1)

where \( \phi \) is the porosity of the medium

\( V_p \) is the non-solid volume (pores and liquid) \([L^3]\)

\( V_m \) is the total volume of material, including the solid and non-solid parts \([L^3]\)

In the saturated zone, which occurs beneath the water table, the porosity is a direct measure of the water contained per unit volume. Porosity is a fraction between 0 and 1, typically ranging from less than 0.01 for solid granite to more than 0.5 for peat and clay. It averages about 0.25 to 0.35 for most aquifer systems (Wikipedia, 2005). In flow and transport studies, it is the flow, or effective, porosity that is relevant.
3.1.2 Hydraulic conductivity, transmissivity and intrinsic permeability

Hydraulic conductivity, $K$ [L.T⁻¹], is a property of the soil that describes the ease with which water can move through pore spaces or fractures. It depends on the intrinsic permeability of the material and on the degree of saturation. Transmissivity, $T$ [L².T⁻¹], is a measure of how much water an aquifer can transmit horizontally. It depends on the aquifer's saturated hydraulic conductivity, $K_s$, and on the saturated thickness of the aquifer $b$:

$$T = K_s \times b$$  \hspace{1cm} (3.2)

Because of their high porosity and permeability, sand and gravel aquifers have higher hydraulic conductivity than clay or unfractured granite aquifer. Sand or gravel and gravel aquifers would thus be easier to extract water from, because of their higher transmissivity, than clay or unfractured granite aquifers (Wikipedia, 2005). Typical values for aquifers would be $10^{-4}$ m.s⁻¹ for sand, $10^{-6}$ m.s⁻¹ for silt and $10^{-7}$ cm.s⁻¹ for clay (Bedient et al., 1999).

Permeability is a measure of the ability of a to transmit fluids through it. The intrinsic permeability $k$ [L²] of a soil is a property of the medium only, independent of fluid properties. It can be related to hydraulic conductivity $K$ by:

$$K = k \left( \frac{\rho g}{\mu} \right)$$  \hspace{1cm} (3.3)

where $\mu$ is the dynamic viscosity [M.L⁻¹.T⁻¹]

$\rho$ is the fluid density [M.L⁻³]

$g$ is the gravitational constant [L.T⁻²]

3.1.3 Storage coefficient

The storage coefficient $S$ is defined as the volume of water that an aquifer releases from or takes into storage per unit surface area per unit change in piezometric head. For a confined aquifer, values of $S$ fall in range of 0.00005 to 0.005, indicating that large pressure changes produce small changes in the storage volume. The storage coefficient for an unconfined aquifer typically ranges from 0.07 to 0.25 (Bedient et al., 1999).

3.1.4 Groundwater flow

The first experimental study of groundwater flow was performed by Henry Darcy in 1856 (Fetter, 1998). He found that, for a one-dimensional flow, the flow rate of water through porous media is proportional to the cross-sectional area and to the head loss.
along the path, and inversely proportional to the length of the flow path. Darcy’s law can be expressed as:

\[ Q = -KA\frac{dh}{dl} \]  \hspace{1cm} (3.4)

where \( Q \) is the volumetric discharge of water \([L^3.T^{-1}]\)

\( K \) is the hydraulic conductivity \([L.T^{-1}]\)

\( A \) is the cross sectional area \([L^2]\)

\( dh / dl \) is the gradient of hydraulic head \([L.L^{-1}]\)

3.1.5 Flow nets

Darcy’s law was originally derived for one dimension, but because many groundwater problems are really two- or three-dimensional, graphical methods are available for the determination of flow rate and direction. A specified set of streamlines and equipotential lines can be constructed for a given set of boundary conditions to form a flow net in two dimension, as shown on Figure 3.1 (Bedient et al, 1999).

Figure 3.1  Example of flow net (source: Broms, 1992).
3.2 Sources and types of groundwater contamination

3.2.1 Sources of contamination

Sources of groundwater contamination are numerous and widespread. More than 30 different potential sources of groundwater contamination were listed by the American Office of Technological Assessment (OPA 1984), divided in six categories, as described Table 3.1.

Table 3.1 Sources of groundwater contamination (source: Bedient et al, 1999).

<table>
<thead>
<tr>
<th>CATEGORY I</th>
<th>CATEGORY II</th>
<th>CATEGORY III</th>
</tr>
</thead>
<tbody>
<tr>
<td>sources designed to discharge substances</td>
<td>Sources designed to store, treat and/or dispose substances</td>
<td>sources designed to retain substances during transport</td>
</tr>
<tr>
<td>Septic tanks and cesspools</td>
<td>Landfills</td>
<td>Pipelines</td>
</tr>
<tr>
<td>Injection wells</td>
<td>Open dumps</td>
<td>Material transport and transfer</td>
</tr>
<tr>
<td>Land application</td>
<td>Residential disposal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Surface impoundments</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mine wastes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Material stockpiles</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Graveyard</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Animal burials</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Above-ground storage tanks</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Underground storage tanks</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Containers</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Open incineration and detonation sites</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Radioactive-waste-disposal sites</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CATEGORY IV</th>
<th>CATEGORY V</th>
<th>CATEGORY VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>sources discharging substances as a consequence of other planned activities</td>
<td>sources providing a conduit for contaminated water to enter aquifer</td>
<td>naturally occurring sources whose discharge is created and/or exacerbated by human activities</td>
</tr>
<tr>
<td>Irrigation</td>
<td>Production wells</td>
<td>Groundwater – surface water interactions</td>
</tr>
<tr>
<td>Pesticide applications</td>
<td>Monitoring wells and exploration borings</td>
<td>Natural leaching</td>
</tr>
<tr>
<td>Fertiliser applications</td>
<td>Construction excavation</td>
<td>Saltwater intrusion</td>
</tr>
<tr>
<td>Farm animal wastes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt application for highway de-icing</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Home water softeners</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urban runoff</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Percolation of atmospheric pollutants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mine drainage</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Highest priority ranking has been given to underground storage tanks, abandoned waste sites, agricultural activities, septic tanks, surface impoundments and municipal landfills, since they are numerous and represent the major threat to groundwater (Bedient et al., 1999). Underground storage tanks are used to store fuel, heating oil, chemicals, liquid hazardous wastes and other products. They represent a high source of groundwater contamination as they can leak through holes due to corrosion or cracks. Either tanks themselves or any associated piping present a risk. Abandoned waste sites are not monitored anymore. Thus, they might not have any leachate-collection system and are highly likely to contaminate groundwater. Agricultural activity includes irrigation, pesticide and fertiliser applications. Chemicals are applied to the crops both to control weeds and pests invasion and to make the land more fertile. When crops are irrigated, the excess water (return flow) can mobilise those chemicals and make them migrate through the soil to the water table. Septic tanks are designed to discharge domestic wastewater into the subsurface above the water table. Septic systems discharge a variety of inorganic and organic compounds, as well as biological pathogens such as bacteria and viruses. Surface impoundments, such as pits, ponds and lagoons, are or were used for storage and/or treatment of both liquid non-hazardous and hazardous waste and the discharge of non-hazardous waste. Landfills were originally designed to reduce the pollution and to minimise the adverse effects of waste disposal. However, particularly the older ones are simply large holes in the ground filled with waste and covered with dust, leaking liquids that are contaminating groundwater. Leachate is formed from the liquids found in the waste as well as by leaching of the solid waste by rainfall.

Some of these sources of contamination are summarised in Figure 3.2.
3.2.2 Types of contamination

A wide variety of contaminants can be found in groundwater, both organic and inorganic. Among those pollutants, we can find synthetic organic chemicals, hydrocarbons, inorganic cations, inorganic anions, pathogens and radionucleides. These materials have different solubility in groundwater. Thus, some organic compounds can be found both in a dissolved form and as an insoluble non-aqueous phase. The inorganic cations and anions, as well as radionucleides, may come from both natural and anthropogenic sources.

3.3 Contaminant transport processes in saturated media

Mass transport is the transport of solutes dissolved in groundwater (Fetter, 1998). These transports are known as advection, diffusion and dispersion.

3.3.1 Transport by advection

Advection is defined as the movement of a solute with the flowing groundwater. The mass flux of dissolved contaminant that is being transported depends on its concentration in groundwater and on the quantity of groundwater flowing. For a one-dimensional flow normal to a cross-sectional area of porous media, this quantity of groundwater equals the average linear velocity times the effective porosity. Thus, for a one-dimensional flow, the mass flux \( F_x \) [M.T\(^{-1}\).L\(^{-2}\)] is given by the following equation:

\[
F_x = v_x n_e C
\]

where \( v_x \) is the average linear velocity [L.T\(^{-1}\)]

\( n_e \) is the effective porosity

\( C \) is the solute concentration [M.L\(^{-3}\)]

The average linear velocity \( v_x \) is the rate at which the flux of water across the unit cross-sectional area of porous media occurs. It is given by the following equation:

\[
v_x = \frac{K}{n_e} \frac{dh}{dl}
\]

where \( K \) is the hydraulic conductivity [L.T\(^{-1}\)]

\( dh / dl \) is the hydraulic gradient [L.L\(^{-1}\)]

The average linear velocity is thus equal to the Darcy velocity divided by the effective porosity associated with the porous medium through which can water flow.
### 3.3.2 Transport by diffusion

Molecular diffusion describes the movement of a solute in water from an area of higher concentration to an area of lower concentration. Diffusion occurs as long as a concentration gradient exists, even if the fluid is not moving, causing spreading and random motion. The mass of fluid diffusing follows the Fick’s first law, which is, in one dimension, given by:

\[
F = -D_d \frac{dC}{dx}
\]  

(3.7)

where \( F \) is the mass flux of solute per unit area \([\text{M.T}^{-1}.\text{L}^{-2}]\)

\( D_d \) is the diffusion coefficient \([\text{L}^2.\text{T}^{-1}]\)

\( C \) is the solute concentration \([\text{M.L}^{-3}]\)

\( \frac{dC}{dx} \) is the concentration gradient \([\text{M.L}^{-3}.\text{L}^{-1}]\)

Values of \( D_d \) are specific for each pollutant and are, among others, temperature-dependent.

If the concentrations are changing with time, Fick’s second law applies, which is, in one dimension:

\[
\frac{\partial C}{\partial t} = D_d \frac{\partial^2 C}{\partial x^2}
\]

(3.8)

where \( \frac{\partial C}{\partial t} \) is the change in concentration with time \([\text{M.L}^{-3}.\text{T}^{-1}]\).

Since diffusion cannot proceed as fast in porous media as in water because of mineral grains, an effective diffusion coefficient \( D^* \) \([\text{L}^2.\text{T}^{-1}]\) has been introduced:

\[
D^* = \omega D_d
\]

(3.9)

where \( \omega \) is the tortuosity coefficient. Tortuosity allows to take into account the effect of the shape of the path followed by water through porous media.

### 3.3.3 Dispersion process

#### 3.3.3.1 Mechanical dispersion

Mechanical dispersion is the transport of a solute resulting from minor differences in groundwater velocity as it flows through heterogeneous porous media. When solutes in groundwater get in contact with water that does not contain a solute, mixing occurs along the flow path, resulting in a dilution of the solute at the advancing edge of flow. Mechanical dispersion can be broken down in two complementary dispersions: longitudinal dispersion (see Figure 3.3), which is the mixing that occurs along the
direction of the flow path, and transverse dispersion, which is the mixing in directions normal to the flow path. Assuming that mechanical dispersion follows Fick’s law for diffusion and that the amount of mechanical dispersion is a function of the average linear velocity, a coefficient of mechanical dispersion has been introduced. This coefficient is defined by:

Coefficient of longitudinal mechanical dispersion = $\alpha_i \bar{v}_i$  \hspace{1cm} (3.10)

where $\bar{v}_i$ is the average linear velocity in the principal direction of flow $i$ [L.T$^{-1}$]

$\alpha_i$ is the dynamic dispersivity in the principal direction of flow $i$ [L]

and

Coefficient of tranverse mechanical dispersion = $\alpha_j \bar{v}_i$  \hspace{1cm} (3.11)

where $\bar{v}_i$ is the average linear velocity in the principal direction of flow $i$ [L.T$^{-1}$]

$\alpha_j$ is the dynamic dispersivity in $j$ direction [L]

Dynamic dispersivity is a property of the medium.

\[D_v D_{Li} = \alpha_i \bar{v}_i + D^*\]  \hspace{1cm} (3.12a)

\[D_v D_{Tj} = \alpha_j \bar{v}_i + D^*\]  \hspace{1cm} (3.12b)

where $D_{Li}$ is the longitudinal hydrodynamic dispersion coefficient [L$^2$.T$^{-1}$]

$D_{Tj}$ is the transverse hydrodynamic dispersion coefficient [L$^2$.T$^{-1}$]

3.3.3.2 Hydrodynamic dispersion

Hydrodynamic is a combination of diffusion and mechanical dispersion in flowing groundwater. The hydrodynamic dispersion coefficient was introduced and defined as follows:

$D_{Li} = \alpha_i \bar{v}_i + D^*$  \hspace{1cm} (3.12a)

$D_{Tj} = \alpha_j \bar{v}_i + D^*$  \hspace{1cm} (3.12b)

Figure 3.3 Factors causing longitudinal mechanical dispersion (source: Cunningham, 2004).

Dynamic dispersivity is a property of the medium.
\( \alpha_L \) is the longitudinal dynamic dispersivity [L]

\( \alpha_T \) is the transverse dynamic dispersivity [L]

### 3.3.4 Mass transport equations

The equation governing transport on groundwater is obtained from the derivation of the advection-dispersion equation. This derivation is based on the law of conservation of mass of solute flux into and out of a small representative elementary volume of the porous media. To apply this derivation, it has to be assumed that the porous medium is homogeneous, isotropic and saturated with fluid. Moreover, it assumed that the flow is steady-state, and that Darcy’s law applies.

The solute is transported both by advection and hydrodynamic dispersion. In the \( i \) direction, the solute transport is given by:

Adveotive transport = \( v_i n_e C dA \)  \hspace{1cm} (3.13)

Dispersive transport = \( n_e D_i \frac{\partial C}{\partial i} dA \)  \hspace{1cm} (3.14)

where \( v_i \) is the average linear velocity in the \( i \) direction [L.T\(^{-1}\)]

\( n_e \) is the effective porosity

\( D_i \) is the hydrodynamic dispersion coefficient in the \( i \) direction [L\(^2\).T\(^{-1}\)]

\( C \) is the solute concentration [M.L\(^{-3}\)]

\( dA \) is the cross-sectional area of the element normal to the \( i \) direction [L\(^2\)]

Since the medium is supposed to be homogeneous, the porosity is considered to be constant. The total mass flux of solute transported in the \( i \) direction per unit of cross-sectional area is then given by:

\[ F_i = v_i n_e C - n_e D_i \frac{\partial C}{\partial i} \] \hspace{1cm} (3.15)

the negative sign indicates that the dispersive flux is from areas of higher to areas of lower concentration.

The difference between flux of solute entering the representative elementary volume and the flux leaving it is \( - \left( \frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z} \right) dx dy dz \). The rate of mass change in the representative elementary volume is \( n_e \frac{\partial C}{\partial t} dx dy dz \). Then, by the law of mass conservation, we have:
\[-\left(\frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}\right) \right\} dx \, dy \, dz = n_e \frac{\partial C}{\partial t} \right\} dx \, dy \, dz \quad (3.16a)\]

i.e.

\[-\left(\frac{\partial F_x}{\partial x} + \frac{\partial F_y}{\partial y} + \frac{\partial F_z}{\partial z}\right) = n_e \frac{\partial C}{\partial t} \quad (3.16a)\]

By substituting the values of $F_x$, $F_y$ and $F_z$ by their expressions in equation (3.17) for each direction $x$, $y$ and $z$, and after cancellation of $n_e$ from both sides, we have:

\[-\left[\frac{\partial}{\partial x} \left( D_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left( D_z \frac{\partial C}{\partial z} \right) \right] = \frac{\partial C}{\partial t} \quad (3.18)\]

Equation (3.18) is the three-dimensional equation of mass transport for a conservative solute. In a homogeneous medium, $D_x$, $D_y$ and $D_z$ do not vary in space and in general, $D_x \neq D_y \neq D_z$. Moreover, the velocity is steady and uniform. Therefore, equation (3.18) becomes:

\[-\left[ D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \right] = \frac{\partial C}{\partial t} \quad (3.19)\]

For one-dimensional flow, the governing equation in a homogeneous, isotropic porous medium reduces to the familiar advective-dispersion equation:

\[ D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad (3.20)\]

while for two-dimensional flow with a direction of flow parallel to the $x$ axis, the equation becomes:

\[ D_L \frac{\partial^2 C}{\partial x^2} + D_T \frac{\partial^2 C}{\partial y^2} - v_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad (3.21)\]

where $D_L$ is the longitudinal hydrodynamic dispersion coefficient [L$^2$.T$^{-1}$]

$D_T$ is the transverse hydrodynamic dispersion coefficient [L$^2$.T$^{-1}$]

### 3.4 Contaminant fate processes

Advection and hydrodynamic dispersion simply redistribute the mass of dissolved contaminants within the geologic material. Neither process changes the amount of...
solute mass in groundwater. However, physical, chemical and biological processes can alter the mass of solute by transforming the solute to another form, moving the solute from the liquid (groundwater) to solid phase (aquifer material) or degrading it.

The one-dimensional advection-dispersion equation (3.20) can be modified to include sorption and decay, the two other global processes that can modify contaminant concentration with time:

\[
\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{B_d}{\theta} \frac{\partial C^*}{\partial t} + \left( \frac{\partial C}{\partial t} \right)_{rxn}
\]  

(3.22)

where \( C \) is the concentration of the solute in the liquid phase [M.L\(^{-3}\)]

\( t \) is the time [T]

\( D_L \) is the longitudinal dispersion coefficient [L\(^2\).T\(^{-1}\)]

\( v_x \) is the average linear groundwater velocity [L.T\(^{-1}\)]

\( B_d \) is the bulk density of aquifer [M.L\(^{-3}\)]

\( \theta \) is the volumetric moisture content or porosity for saturated media

\( C^* \) is the amount of solute sorbed per unit weight of solid [M.m\(^{-1}\)]

\( rxn \) is the subscript indicating a biological or chemical reaction of the solute (other than sorption)

### 3.4.1 Sorption and desorption processes

Sorption is defined as the association of a dissolved or gaseous contaminant with a solid material (Bedient et al., 1999). The term of sorption encompasses two more specific processes known as adsorption and absorption. Adsorption is the association of a contaminant with the surface of a solid particle. Absorption is the association of a contaminant within a solid particle. Sorption processes also include chemisorption and ion exchange. Chemisorption occurs when the solute is incorporated on solid particle surface by a chemical reaction. Cation exchange can occur when a cation is attracted to the region close to a negatively charged clay mineral-surface and held there by electrostatic forces. Anion exchange can occur at positively charged sites of iron and aluminum oxides sand the broken edges of clay minerals (Fetter, 1998). The reverse process of sorption is desorption. It is the dissociation of a sorbed molecule and its return to the aqueous or gaseous phase.

Sorption is an important process affecting the transport of contaminants in groundwater since the solutes will move more slowly through aquifer. This effect is
called retardation and can affect the ability to remediate contaminated sites. The distribution of a contaminant between either the aqueous or the solid phase is called partitioning. Local equilibrium of the distribution of the contaminant between those two phases often exists. Thus, there is a direct, linear relationship between the amount of solute sorbed onto solid and the concentration of the solute in the liquid phase, defining the partition coefficient $K_d$:

$$K_d = \frac{C^*}{C}$$  \hspace{1cm} (3.23)

where $K_d$ is the partition coefficient (or distribution coefficient) \([L^3.M^{-1}]\)

$C^*$ is the mass of solute sorbed per unit weight of solid \([M. M^{-1}]\)

$C$ is the concentration of the solute in solution in equilibrium with the mass of solute sorbed onto the solid \([M.L^{-3}]\)

By replacing the value of $C^*$ by its expression $K_d C$ in equation (3.22) and assuming that there is no biological or chemical reaction of the solute other than sorption, we obtain:

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{B_d}{\theta} \frac{\partial (K_d C)}{\partial t}$$  \hspace{1cm} (3.24)

which can also be written:

$$\frac{\partial C}{\partial t} \left(1 + \frac{B_d}{\theta} K_d\right) = D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x}$$  \hspace{1cm} (3.25)

The term $1 + \frac{B_d}{\theta} K_d$ is called retardation factor and is written $r_f$.

If the average linear groundwater velocity is $v_x$, the average velocity of the solute front where the concentration is one-half of the original, $v_c$, is then given by (Fetter, 1998):

$$v_c = \frac{v_x}{r_f}$$  \hspace{1cm} (3.26)

### 3.4.2 Abiotic transformation

#### 3.4.2.1 Hydrolysis

Hydrolysis refers to a chemical reaction between a contaminant molecule and water. This process is important for certain contaminants, including alkyl halides, carboxylic acid esters and carboxylic acid amides (Bedient et al, 1999). Water reacts with the
compounds to substitute an OH$^-$ for an X$^-$, crating an alcohol. The rate that a chemical undergoes hydrolysis is strongly temperature and pH dependent.

3.4.2.2 Oxidation-Reduction

Oxidation-reduction reactions involve the transfer of electrons between a contaminant molecule and another chemical species. A gain of electron is called a reduction while a loss of electron is called oxidation. Some micro-organisms may act as catalysts for the reaction. Therefore, biologically mediated oxidation-reduction reactions are more rapid than abiotic reactions for many contaminants in groundwater. Thus, abiotic oxidation-reduction are often neglected in transport calculations (Bedient et al., 1999).

3.4.2.3 Elimination

Elimination reactions occur with a specific group of groundwater contaminants, in particular halogenated ethanes and propanes. For these chemicals, elimination reactions are characterised by the release of a halogen group and a proton from adjacent carbon atoms with the subsequent formation of a carbon-carbon bond (Bedient et al., 1999).

3.4.3 Biodegradation

Biodegradation occurs when a contaminant is completely converted to mineralised end products (i.e. CO$_2$, H$_2$O and salts) through metabolism by living organisms. In groundwater systems, the organisms that carry out this process are bacteria indigenous to the aquifer. In some cases, metabolic activity does change the chemical form of the contaminant but does not result in the mineralisation. This processes are then called biotransformation.

3.5 Flow and mass transport in the water-unsaturated zone

Flow and transport mechanisms in the unsaturated zone are much more complex than in the saturated zone due to the effect of capillary forces and non-linear soil characteristics. In a unsaturated porous medium, part of the pore space is filled with water and part is filled with air. The amount of moisture in a soil can be expressed either as the gravimetric water content $w$ (weight of the water as a ratio to the weight of the dry soil mass), or as the volumetric water content $\theta_w$ (volume of water as the ratio to the total volume of the soil mass). By defining $\theta_a$ as the volume of air as a ratio to the total volume of the soil mass, then the total porosity of the porous medium is given by the sum of the two moisture contents:
\[ n = \theta_w + \theta_a \]  

(3.27)

where \( n \) is the total porosity of the porous medium.

### 3.5.1 Flow of water in the unsaturated zone

The presence of air in the pore space makes vadose zone hydrology different from saturated zone hydrology. The hydraulic properties of the porous media vary with the relative proportion of air and water in the pores.

#### 3.5.1.1 Unsaturated hydraulic conductivity

Darcy’s law is still valid for unsaturated flow, except that hydraulic conductivity is now a function of the water content of the soil:

\[
K(\theta) = -\frac{\nu}{\frac{\partial h}{\partial z}}
\]  

(3.28)

with

\[ h = z + \psi \]  

(3.29)

where \( K(\theta) \) is the unsaturated hydraulic conductivity \([L.T^{-1}]\)

- \(\nu\) is darcy velocity \([L.T^{-1}]\)
- \(z\) is the depth below the surface \([L]\)
- \(h\) is the potential or head \([L]\)
- \(\psi\) is the tension or capillary suction \([L]\)
- \(\theta\) is the volumetric moisture content

Both \(\theta\) and \( K \) are functions of the capillary suction \(\psi\). \(\psi\) is also called capillary potential or matric potential, and it represents the negative pressure at all points above the water table in the pores of unsaturated porous media. This pressure becomes positive for points below the water table.

#### 3.5.1.2 Soil-water characteristic curves

Soil-water characteristic curves represent the volumetric water content according to the matric potential for a particular soil (see Figure 3.4). At atmospheric pressure, the soil is saturated with water content equal to \(\theta_s\). The soil will remain saturated as the
matric potential is gradually decreased. Eventually, the matric potential will become negative enough for the water to begin to drain from soil. This matric potential value is called bubbling pressure. The moisture content will continue to decline as the matric pressure is lowered, until it reaches some irreducible minimum water content $\theta_r$. Further reduction of the matric potential would not result in the loss of any additional moisture (Fetter, 1998). One of the simple empirical expression that can be used to relate the water content of a soil to the matric potential is Brooks and Corey’s relationship:

$$\theta = \theta_s + \left( \theta_s - \theta_r \right) \left( \frac{\psi}{h_b} \right)^{-\lambda}$$

where $\theta$ is the volumetric water content

$\theta_s$ is the volumetric water content at saturation

$\theta_r$ is the irreducible minimum water content

$\psi$ is the matric potential [L]

$h_b$ is the bubbling pressure [L]

$\lambda$ is an experimentally derived parameter

Brooks and Corey also defined an effective saturation $S_e$ as:

$$S_e = \frac{S_w - \theta_r}{1 - \theta_r}$$

where $S_w$ is the saturation ratio $\theta / \theta_s$

Van Genuchten also derived an empirical relationship between capillary pressure and volumetric water content:

$$\theta = \theta_s + \frac{\theta_s - \theta_r}{\left[ 1 + \left( \frac{\psi}{\psi_b} \right)^n \right]^m}$$

where $\alpha$, $n$ and $m$ are constants.

Generally, these equations work well for medium- and coarse-textured soils with predictions for fine-textured materials usually being less accurate. These equations are often used in computer models to represent soil characteristics for flow in the vadose zone. For large capillary heads, the Brooks and Corey and Van Genuchten models become identical if $\lambda = mn$ and $\psi_b = 1 / \alpha$. 
3.5.1.3 Governing equation for unsaturated flow

The unsaturated continuity equation represents the fact that the change in total volumetric water content with time in a representative elementary volume of the unsaturated zone is equal to the sum of any change in the flux of water into and out of the representative volume:

\[
\frac{\partial \theta}{\partial t} = \left( \frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z} \right)
\]  

(3.33)

where \( q_x, q_y, \) and \( q_z \) are soil moisture fluxes. By substituting Darcy’s law equation \((3.28)\) into unsaturated continuity equation, the following result is obtained:

\[
\frac{\partial \theta}{\partial t} = -\frac{\partial}{\partial z} \left[ K(\theta) \frac{\partial \psi(\theta)}{\partial z} \right] - \frac{\partial K(\theta)}{\partial z}
\]  

(3.34)

where \( \theta \) is the volumetric moisture content

\( z \) is the distance below the surface [L]

\( \psi \) is the matric potential [L]

\( K(\theta) \) is the unsaturated hydraulic conductivity [L.T\(^{-1}\)]

This equation is called Richards equation. It assumes that water is incompressible, that the soil matrix is non-deformable and that the presence of air can be ignored unless it affects the value of \( K \). It is a non-linear equation that is quite difficult to solve by analytical means, but some numerical methods of solution have been developed.
3.5.2 Mass transport in the unsaturated zone

The total one-dimension solute flux in an unsaturated zone is the result of advection, diffusion and hydrodynamic dispersion. With diffusion and hydrodynamic dispersion combined as the soil-moisture dispersion coefficient, the result can be expressed as:

\[ J = v \theta C - D_s \theta \frac{dC}{dz} \quad (3.35) \]

where \( J \) is the total mass of solute across a unit cross-sectional area in a unit of time \([M.L^{-2}.T^{-1}]\)

\( v \) is the average soil moisture velocity \([L.T^{-1}]\)

\( \theta \) is the volumetric water content

\( C \) is the solute concentration in the soil moisture \([M.L^{-3}]\)

\( dC/dz \) is the solute gradient \([M.L^{-3}.L^{-1}]\)

\( D_s \) is the soil moisture diffusion coefficient, which is a function of both \( \theta \) and \( v \) \([L^2.T^{-1}]\)

The continuity equation for a solute is given by:

\[ \frac{\partial (B_d C^*)}{\partial t} + \frac{\partial (\theta C)}{\partial t} = -\frac{\partial J}{\partial z} \quad (3.36) \]

where \( B_d \) is the soil bulk density \([M.L^{-3}]\)

\( C^* \) is the concentration of the solute phase bound to the soil

By combining equations (3.35) and (3.36), we obtain:

\[ \frac{\partial (B_d C^*)}{\partial t} + \frac{\partial (\theta C)}{\partial t} = \frac{\partial (v \theta C)}{\partial z} + \frac{\partial}{\partial z} \left( D_s \theta \frac{\partial C}{\partial z} \right) \quad (3.37) \]

In order to obtain the fundamental mass transport equation for the vadose zone, sources and sinks of solute must be taken into account. These can be added to equation (3.34) by means of term for the summation of \( \gamma \), where \( \gamma \) represents other sources and sinks:

\[ \frac{\partial (B_d C^*)}{\partial t} + \frac{\partial (\theta C)}{\partial t} = \frac{\partial}{\partial z} \left( D_s \theta \frac{\partial C}{\partial z} - qC \right) + \sum_i \gamma_i \quad (3.38) \]

where \( q \) is the convective soil moisture flux \( (q = v \theta) \) \([L.T^{-1}]\)
If $B_d$, $D_s$, $\theta$ and $q$ are considered to be constant in time and in space, then equation (3.38) reduces to equation (3.22), which is the basic one-dimensional advection-dispersion equation.

### 3.6 Numerical modelling approach of groundwater flows and transport systems

Before remediating contaminated groundwater of a specified field, it is necessary to understand the physical, chemical and biological processes that occur in the field. By translating these processes into mathematical terms, groundwater modelling is a tool designed to represent a simplified version of a real field site, and therefore allows to understand and predict the system and its behaviour. The resulting model is only as good as the conceptual understanding of the processes. The goal of modelling is to predict the value of an unknown variable such as head in an aquifer system or the concentration distribution of a given chemical in the aquifer in time and space.

Modelling groundwater contaminant transport involves three initial considerations: model selection (development of a conceptual model and translation of this conceptual model into mathematical model), solution technique (analytical or numerical model), and input data. The conceptual model consists of a description of the physical, chemical and biological processes which are thought to be governing the behaviour of the system. Therefore, model selection involves selection of the type of processes to be studied and included in the mathematical statement. Different solution techniques are available to solve the chosen mathematical model. Analytical solution are usually possible only for simple geometries, homogeneous aquifers and simple boundary conditions. A computer that implements the numerical model is referred as a computer code or computer model. Computer models are essential to analyse subsurface flow and contamination problems because they are designed to incorporate hydrologic parameters that an analytical model cannot incorporate. Finally, a great quantity of input data for the model must be gathered from a literature review, field investigations, and/or laboratory studies (Mehnert and Hensel, 1996; Bedient et al, 1999).

Nowadays, three of the most developed and used groundwater modelling softwares are Groundwater Modeling System (GMS), Groundwater Vistas (GV) and Visual MODFLOW. According to Software User Groups in Groundwater Modelling, GV is a sophisticated Windows graphical user interface for 3D groundwater flow and transport modelling, and Visual MODFLOW is a proven standard for professional 3D groundwater flow and contaminant transport modelling (SSG, 2005). GMS will be described in the following part. All of these three softwares use the same packages (see GMS description) but with different codes, interfaces and presentations.
4 Methodology

Description of GMS

GMS is said to be the most advanced, powerful and comprehensive groundwater modelling software available nowadays. It provides an integrated and comprehensive computational environment for simulating subsurface flow, contaminant fate and transport, and the efficacy and design of remediation systems. GMS integrates and simplifies the process of groundwater flow and transport modelling by bringing together all of the tools needed to complete a successful study. It provides a comprehensive graphical environment for numerical modelling, tools for site characterisation, model conceptualisation, mesh and grid generation, geostatistics, and sophisticated tools for graphical visualisation. GMS supports both finite-difference and finite-element models in 2D and 3D including MODFLOW 2000, MODPATH, MT3DMS/RT3D, SEAM3D, ART3D, UTCHEM, FEMWATER, PEST, UCODE, MODAEM and SEEP2D (SSG, 2005; CHL, 2005). GMS has been developed by the Environmental Modeling Research Laboratory (EMRL), in the USA.

4.1 Groundwater flow modelling with MODFLOW

Description of MODFLOW

MODFLOW is the name that has been given to the USGS Modular Three-Dimensional Groundwater Flow Model developed in 1988 (McDonald and Harbaugh, 1988). Because of its ability to simulate a wide variety of systems, its extensive publicly available documentation, and its rigorous USGS peer review, MODFLOW has become the world-wide standard groundwater flow model. It is used to simulate systems for water supply, containment remediation and mine dewatering. When properly applied, MODFLOW is the recognised standard model used by courts, regulatory agencies, universities, consultants and industries.

MODFLOW is most appropriate in those situations where a relatively precise understanding of the flow system is needed to make a decision. MODFLOW was developed using the finite-difference method. This method permits a physical explanation of the concepts used in construction of the model. Therefore, MODFLOW is easily learned and modified to represent more complex features of the flow system. Layers can be simulated as confined, unconfined, or a combination of both. Flows from external stresses such as flow to wells, areal recharge, evapotranspiration, flow to drains, and flow through riverbeds can also be simulated. A large amount of information and a complete description of the flow system is thus required to make the most efficient use of MODFLOW. In situations where only rough estimates of the flow system are needed, the input requirements of MODFLOW may not justify its use. To use MODFLOW, the region to be simulated must be divided into cells with a rectilinear grid resulting in layers, rows and columns. Files must then be prepared that contain hydraulic parameters (hydraulic conductivity, transmissivity, specific yield, etc.), boundary conditions (location of impermeable boundaries and constant heads), and stresses (pumping wells, recharge from precipitation, rivers, drains, etc.) (SSG, 2005).
1st step: constant head

The first step of the groundwater flow modelling was to build some realistic piezometric map of the field for some fixed dates (depending on the available data). In order to achieve a realistic interpolation of the groundwater level in the field, several intrinsic data had to be known: the head of several points spread all over the field, the recharge of the area and the hydraulic conductivity of the different layers. Since these data are partly assumed or interpolated, they would have to be adapted in order to calibrate the model on a realistic situation.

Some head measurements have been carried out and several set of data are available. For four specific days (February 5th, 2002, February 14th, 2002, September 24th, 2002 and November 29th, 2004), the groundwater level of several spots in the field are known (see Figure 2.3 for the distribution of the observation wells). In a first simulation, the hydraulic conductivity has be assumed to be $1.3 \cdot 10^{-4} \text{ m.s}^{-1}$ ($232 \text{ m.day}^{-1}$) for the filling material and 10 000 times less for the marine clay ($0.001 \text{ m.day}^{-1}$). These values were obtained during a previous study of the area. The value of the recharge has been estimated according to the precipitation and evaporation maps of Sweden. The mean value of precipitation in the Göteborg area is 900 mm.year$^{-1}$ and the mean value of the evaporation in the field area was assumed to be 400 mm.year$^{-1}$ (due to the low presence of vegetation in the field). Therefore, the recharge for the area has been estimated to be 500 mm.year$^{-1}$ ($1.37 \cdot 10^{-4} \text{ m.day}^{-1}$).

Two approaches can be used to construct a MODFLOW simulation with GMS: the grid approach or the conceptual model approach. In this case, the conceptual model approach was used since it involves using the Geographical Information Systems (GIS) tools in the Map module to develop a conceptual model of the site being modelled. The location of sources/sinks, layer parameters such as hydraulic conductivity, model boundaries, and all other data necessary for the simulation can be defined at the conceptual model level. Once this model is complete, the grid is generated and the conceptual model is converted to the grid model and all of the cell-by-cell assignments are performed automatically (EMRL, 2003). A map of the Wockatz field was available on a *.dxf format and was used as the background.

After having imported the background map in GMS, the conceptual model has been build using points, nodes, arcs and polygons. Arches have been used to delimit the boundaries of the area. The western boundary has been defined as “river”. Each known head has been entered as “specified constant head” for their specific spots. The recharge and the hydraulic conductivity values have been entered and a $50 \times 50$ cells grid has been built. First, only two layers have been defined, one for each type of soil. The first layer, with a bottom elevation of 10 m and a top elevation of 14 m, represents the filling material, whereas the second one, between 5 m and 10 m, represents the marine clay. The grid has been activated and the model could be run. A piezometric map has been obtained for each of the four sets of data.

2nd step: transient head, annual variation

Since the purpose of the simulations was to obtain a contaminant transport modelling on a rather long term, and given that the groundwater level is not constant all year
long, it was interesting to obtain a modelling of the transient groundwater head for the area. For this, and because of the limited source of data, the assumption was made that the groundwater head varies annually and that the variation is the same every year. Therefore, all the data could be used, assuming that they collectively represent the variation of a year.

The process is quite similar to the previous step, except that for each specific spot, the head has entered as “specified transient head” instead of “specified constant head”. The model has been run for a one-year period and a set of piezometric maps showing the groundwater level variation all along the year has been obtained (one map every 30 days). For a better modelling, the maps can also be presented as a film loop.

Encountered difficulties and problems:

Applying a new software is not easy. Since these first steps of the modelling were also the first uses of the software, several parameters or stages were sometimes left out, preventing the modelling from being run properly and from obtaining satisfactory results. Difficulties were especially encountered for the transient groundwater head simulation because a decisive stage has been omitted (to convert the conceptual model from a high-level feature object-based definition to a grid-based MODFLOW numerical model, after having defined the stress periods of the simulation).

Issues to think about:

- In order to get a better representation of the real stratigraphy of the soil (between 50 cm and 1 m of filling material on top of marine clay), it would be interesting to build a modelling with a number of layers greater than the two used. Indeed, in these first simulations, a 4 m layer of filling material has been used, which is much thicker than in the reality. On the new added layers, the groundwater table will have to be observed in order to be able to find the approximate boundary between the filling material and the clay. Once this limit is detected, the hydraulic conductivity can be properly assigned for each defined type of soil.

- In order to build a more realistic and more accurate modelling, it would be interesting to take into account the heterogeneity of the hydraulic conductivity instead of assigning a constant and homogeneous $K$ value for the whole filling material layer. The variability of the hydraulic conductivity can be either obtained from grain size data of the site, if available (using the Hazen formula to calculate the hydraulic conductivity for several spots and then interpolating the obtained set of obtained data all over the concerned area), or directly generated by the software itself (giving some information about the different materials that make up the filling material).

- Because of the lack of available data for the Wockatz site, recharge has been included in the modelling as a constant value for the whole year and the whole length of the simulations. In order to obtain a more realistic modelling, it would be interesting to try to get some data about rainfalls variations in the Wockatz area.
(or at least in Göteborg is nothing more specific is available), and then to deduce
the transient recharge for the site.

- The northern, the eastern and the southern boundaries of the modelling has been
defined so as to coincide with the real borders of the field. Absolutely no
information about the outside of the site have been entered in the modelling.
Thus, modelling has been run considering that no flow was crossing the
boundaries, for the software is not able to compute what happens beyond the
boundaries. However, in the reality, nor fence neither property boundary prevents
the flow from crossing the boundaries of the site. Therefore, it would be
interesting to build a modelling with a larger grid and boundaries situated far
enough from the site for the flow not to be influenced by a virtual barrier.

4.2 Contaminant transport modelling with MT3DMS

Description of MT3DMS

MT3DMS is a comprehensive three-dimensional numerical model for simulating
solute transport in complex hydrogeologic settings that was developed in 1998 (Zheng
and Wang, 1998). It has a modular design that permits simulation of transport
processes independently or jointly. MT3DMS is capable of modelling advection in
complex steady-state and transient flow fields, anisotropic dispersion, and chemical
reactions of dissolved constituents in groundwater systems. It uses a modular structure
similar to the structure utilised by MODFLOW. MT3DMS is used in conjunction with
MODFLOW in a two-step flow and transport simulation. Heads and cell by cell flux
terms are computed by MODFLOW during the flow simulation and are written to a
specially formatted output file. This file is then read by MT3DMS and utilised as the
flow field for the transport portion of the simulation. MT3DMS is a newer version of
the MT3D model developed in 1990 and distributed with earlier versions of GMS.
MT3DMS differs from MT3D in that it allows for multi-species transport, supports
additional solvers, and allows for cell by cell input of all model parameters (SSG,
2005).

1st step: constant head, constant concentration

The first step of the contaminant transport modelling was to observe the contaminant
spread over the field with a constant groundwater head. Contaminant load data are
available only for two of the fixed days (February 5th, 2002 and November 29th,
2004). For these days, the contaminant concentration in groundwater is known for
some specific spots. In order to use MT3DMS properly and to get the most realistic
modelling, some other intrinsic parameters both of the soil and of the contaminants
have to be known, such as the soil density and porosity, the dispersivity and the
partition coefficient $K_d$. It was chosen to study 4 contaminants (cadmium, zinc, lead
and copper) since they are considered to be the most dangerous for human health and
they also exhibit the highest concentrations.
For each of these pollutants, the conceptual model approach of MT3DMS has been used and the model has been run for a period of 3000 days. The advection, dispersion, source/sink mixing, chemical reaction and GCG solver packages have been included in the modelling. The porosity has been assumed to be 0.3 for the first layer (filling material) and 0.04 for the second layer (marine clay). The apparent longitudinal dispersivity $\alpha_L$ is scale dependent and can be estimated by the following relationship (Xu and Eckstein formula, 1995): $\alpha_L = 0.83(\log L)^{2.414}$, where $L$ is the length of the scale. Since the scale we are interested in for the observations is the cell scale, $L$ as been associated to the length of a cell (approximately 3 m), and thus the longitudinal dispersivity has been estimated to be 0.14 m. The ratios of transverse and vertical dispersivity to the longitudinal dispersivity have been assumed to be 1 for both layers. The sorption model that has been used is the linear isotherm one. The bulk density of the filling material has been estimated to be 1.8 g.cm$^{-3}$ ($1.8 \cdot 10^8$ mg.m$^{-3}$) and the bulk density of the marine clay around 2 g.cm$^{-3}$ ($2 \cdot 10^9$ mg.m$^{-3}$). Partition coefficients are very soil-specific. However, nor grain size neither $K_d$ value data were available for the concerned area. Therefore, very generalised approximations of $K_d$ have been used for the modelling. Each known head has been entered as “specified constant head” and each known contaminant concentration has been entered as “constant contaminant concentration” for their specific spots. The model has been run (first MODFLOW then MT3DMS) and several maps were obtained showing the contaminants spread (one map for each 30 days). For a better visualisation, the maps can also be presented as a film loop.

2nd step: transient head, concentration

The final step of the modelling was to combine both the annual groundwater head variation and the contaminant transport, so that all the physical, chemical and biological processes were taken into account. For this, the annual groundwater head variation modelling has been used and the simulation has been extended to 10 years. Then, all what is described for the previous step has been applied to this model, and a contaminant transport modelling has be obtained for the Wockatz area, taking into account the groundwater head variation over the seasons.

Issues to think about:

- The concentrations data have been included in the model as “constant contaminant concentration” for the few spots where the concentration is know on specific days. But those values are quite low and the contaminant transport occurs in a rather important groundwater volume. Thus, according to the MT3DMS simulation, contaminant concentrations tend to decrease very quickly and even almost to disappear after few days, probably due to a quasi immediate dilution of the contaminants, which is not realistic. Therefore, it would be interesting to run an interpolation of the known concentration data on the whole concerned area before using them in the transport modelling. This should be an improvement on two levels. First, the contamination distribution modelling would be much more
realistic than few polluted spots scattered in a non polluted area (concentration default value is 0 mg.l$^{-1}$). Secondly, dilution should not be as important as in the previous case (or even non-existent) and contaminant transport would be the main process.

4.3 Building a more accurate model

4.3.1 4-layer model

As explained before, it was interesting to build a model with more than 2 layers in order to get a better representation of the real geology of the soil. Since the filling material is roughly between 50 cm and 1 m, and given that the maximum observed groundwater head is a bit higher than 12.5 m, it was first thought to modify the model as shown in Figure 4.1.

![Figure 4.1 First approach of the filling material/clay distribution](image)

The first idea was to divide the first layer into 5 layers, with 4 layers 50 cm thick and the last one 2 m thick. Thus, a 6-layer model would be obtained. To identify the boundary between filling material and clay, the highest observed water table was used. The purpose was to have a distance ranging between 50 cm and 1 m between the groundwater table and the clay layers (or cells if the layers were not complete). Thus it could have been possible to have a first idea of the number of columns (in the j direction) that would be assigned with the clay characteristics for all layers.

But by applying the model described above, a problem occurred when running the simulation: the solution was not converging. Indeed, during the dry period, since the groundwater head can be almost 2 m below the highest level, the groundwater table is,
in some parts, below the filling material level, i.e. in the clay. Under these conditions, the model cannot converge. Therefore, the lowest groundwater was accounted for (during the dry period). This time, the purpose was to have a distance between the groundwater table and the clay cells of about 50 cm, so that when the groundwater level rises, the saturated filling material would be ranging between 50 cm and about 2 m. This value, is a bit higher than in reality, but since the groundwater head varies up to 2 m in some parts, it is impossible to keep a thickness between 50 cm and 1 m of saturated filling material for the whole year.

Finally, by adapting the hydraulic conductivity for each type of soil as described above, a 4-layer model that was obtained instead of 6-layer model: the three first layers were only assigned with filling material properties, while layers 4 and 5 were made up with both filling material (close to the river) and clay (on the eastern side). The sixth layer was still assigned only with clay characteristics.

This new 4-layer modelling has been run and, as previously, a set of piezometric maps showing the groundwater level variation has been obtained. This set of maps could then have been compared with the 2-layer model.

4.3.2 Interpolating the concentrations

As explained before, concentrations data were used as “constant contaminant concentration” for scattered spots. Because of those low localised concentration values injected in a significant groundwater volume, almost immediate dilution of pollutants in groundwater occurred, which does not reflect the reality. Therefore, it was interesting to perform an interpolation of the concentrations on the overall concerned area before running the contaminant transport modelling. For this, the 2D geostatistics module has been used. Only few points, non evenly scattered on the site, were available for the interpolation, but this is quite typical from hydrogeological data set and studies.

A text file with the sample points ID, their coordinates and the concentrations of the concerned pollutant has been created for each of the four pollutants. Each text file has been imported as the scatter point set that necessary to run the interpolation. Ordinary kriging interpolation was used since it is supposed to lead to the most realistic model. An experimental variogram has been created, adapting the lag distance and the lag tolerance in order to get the best one. Then, once it has been computed, the next step was to define a model variogram, i.e. a mathematical function that models the trend in the experimental variogram. A gaussian model function has been chosen, adapting the nugget, the contribution and the range in order to get a reasonable fit between the model and at least first part of the experimental variogram (the second part is difficult to fit because of the many zero concentration values that tend to pull the experimental variogram back down). The model variogram is the one used in the kriging computations (EMRL, 2003). The following figure represents the experimental variogram and the model variogram that have been created and used for zinc concentration interpolation.
4.3.3 Selecting the correct set of data to use

Because of the intensive use of the site when it was in operation, it is supposed that the soil is still saturated with contaminants. Therefore, groundwater contamination mainly comes from “leakage” or unloading from the soil. This unloading is directly linked with the amount of water that flows through the site, i.e. with recharge. Thus, since rainfalls vary annually, it is assumed that there is a permanent discharge of contaminants in groundwater with an annual variation. Hence, to build a realistic model, it would have been interesting, as for head data, to use all the data (whatever the year of the samplings), as “transient contaminant concentration”.

However, only 2004 data are reliable, since 2002 samples have not been filtrated before the metal concentrations were measured. Therefore the obtained data do not represent the dissolved metal concentrations and are much higher than expected. Thus, 2002 data cannot be used with 2004 data. Consequently, there is only one concentration measurement that is available for each spot and for each contaminant. Even if this value was entered as “transient contaminant concentration”, it would be interpreted as a constant concentration. Then, modelling of the contaminant transport process would be insignificant compared with the constant imposed concentration value, and even on a large time scale simulation, contaminant transport would not be perceptible.

Moreover, before entering contaminant concentration data in the model, interpolations have been run and the results could only be used in the contaminant transport modelling as “starting concentrations” data set. Thus, concentration data have been used as initial concentrations, and since the process of contamination leakage from soil to groundwater might go on for probably hundreds of years, the final simulation models what would happen if the upper layer of filling material was removed and replaced by a non-contaminated soil layer with more or less the same hydraulic
characteristics. For this scenario, there would be no more contaminant leakage from the saturated parts of the soil. Contaminant transport would thus be the most significant process that would occur.

4.3.4 Assigning a transient recharge

No data is available concerning recharge in the Wockatz area. However, some rainfalls data are accessible on the Göteborg Stad Miljö web site. On this web site, rainfalls for each day, hour by hour, can be found from January 1st, 2002, until today, for the measurement station of Lejonet (at the North East of Göteborg’s Centrum, between 1.5 and 2 km from Wockatz area). From these data, rainfalls have been calculated for each month, in mm.m².month⁻¹ first, then in m.m².day⁻¹ to correspond to the units used in GMS modellings. In order to keep a reasonable proportion of evapotranspiration, 45% of the rainfalls value have been subtracted to get the recharge value. Figure 4.3 shows the recharge variation that has been obtained for 2004.

![2004 recharge](image)

Figure 4.3 Recharge variation for 2004 (source: Göteborg Stad Miljö, 2004).

Since these values are not exactly the ones for the Wockatz area, there was no need to be more accurate for the other years. Thus, assumption has been made that the recharge variation was approximately the same for every year, and 2004 data have been used for the 10 years of modelling. Recharge has been entered in the modelling as “transient recharge” and modellings could be run and compared with the ones previously obtained.

4.3.5 Creating a larger grid

To avoid problems of boundary conditions, it was necessary to build a larger grid modelling with boundaries far enough from the site borders. Indeed, no flow can cross the model boundaries, while it is not the case in the reality. Thus, modelling
boundaries have been moved back to the extremity of the available map, as shown in Figure 4.4.

![Figure 4.4 “Small grid” model and “large grid” model.](image)

The large grid is a $61 \times 96$ cells to keep approximately $3 \text{ m} \times 3 \text{ m}$ cells dimension. Four layers have been defined in the $z$ direction.

Since creating the grid frame and the grid itself is one of the first steps on the modelling, the whole model was rebuilt, applying directly the improvements that have been described above.

### 4.3.6 Generating a heterogeneous hydraulic conductivity for the filling material

Finally, grain size data from Wockatz site were not available in time to be used in the modelling. Thus, in order to take into account the heterogeneity of the filling material layer, and thus the heterogeneity of its hydraulic conductivity, this had to be generated by the software itself, using the T-PROGS software package in the Borehole Module of GMS. T-PROGS can perform transition probability geostatistics to generate multiple equally probable models of aquifer heterogeneity, all of which can be conditioned on borehole data (EMRL, 2003). In this case, boreholes do not exist in the model, so an unconditioned simulation was generated.

The first step in the T-PROGS interface is to define the materials to use for the material set generation. A maximum of five materials can be used in the T-PROGS algorithm. Since there is no specified data for the composition of the filling material in the Wockatz area, the material set generation will be only experimental to check the
influence of the heterogeneity of the soil on the groundwater flow. Up to then, the mean hydraulic conductivity value that has been used for filling material was $1.3 \times 10^{-4} \text{ m.s}^{-1}$ ($11.232 \text{ m.day}^{-1}$). A log-normal distribution of the materials was used with hydraulic conductivity ranging between $10^{-5}$ and $10^{-3}$ m.s$^{-1}$: gravel ($K = 8 \times 10^{-4}$ m.s$^{-1}$), coarse sand ($K = 5 \times 10^{-4}$ m.s$^{-1}$), medium sand ($K = 2.7 \times 10^{-4}$ m.s$^{-1}$), fine sand ($K = 5 \times 10^{-5}$ m.s$^{-1}$), and silt ($K = 2 \times 10^{-5}$ m.s$^{-1}$). Fine sand has been chosen as the background material. Then, vertical and lateral transition trends have to be defined with the vertical, strike and dip Markov chains. Proportion of each material had to be entered and was defined as follows: 2% of gravel, 5% of coarse sand, 10% of medium sand, 53% of fine sand and 30% of silt. The K-values assigned to the materials and the proportions of the materials represented collectively a log-normal distribution with mean value of $1.3 \times 10^{-4}$ m.s$^{-1}$ and a 99% range between $10^{-5}$ m.s$^{-1}$ and $10^{-3}$ m.s$^{-1}$. Markov chains have been generated using the “Edit maximum entropy factors” option, which is ideally suited for cases without borehole data. The lens lengths were assigned to 0.5 m for the vertical transition trends and to 10 m for the lateral transition trends. For further description on the use of T-PROGS, see EMRL (2003) (Tutorials, vol.1).

T-PROGS has been run with 1 iteration and a maximum of 4 quenching iterations, and the following material set generation was obtained:

![Figure 4.5 Heterogeneous material set generation.](image-url)
Unfortunately, because of a problem that has not been solved due to a lack of time, the material set generation could only be run on one background layer. It means that the material set is not varying with $Z$ (the soil is vertical uniform). Nevertheless, a new model has been built with this material distribution. The purpose was to rebuild a 4-layer modelling, as described before. But by using the same distribution as the one used for the previous model, the simulation cannot converge. Once more, the time frame did not allow to solve this problem and to find the new distribution between clay and filling material. Therefore, only a 2-layer modelling has been performed, with a homogeneous hydraulic conductivity for the lower layer, presenting clay, and the heterogeneous hydraulic conductivity that has been generated for the upper layer, representing filling material. The use of the heterogeneous model is still assumed to be valuable for illustrating the differences between a homogeneous and a heterogeneous representation of the hydraulic conductivity.
5 Results and analysis

In this part, results will be presented in the same order they were obtained. By doing so, it can clearly be explained what were the eventual problems and how to improve the modelling. Transport results will be presented only for 2004 concentration data since they are the only ones that are reliable. Except for final results that will be presented for all of the four studied pollutants, intermediate results will be presented only for zinc.

5.1 Evolution of the obtained results

5.1.1 Flow modelling

The first results that have been obtained are piezometric maps (constant head) for the four fixed dates. Figure 5.1 and Figure 5.2 show these piezometric maps for February 5th, 2002, and November 29th, 2004. The purple spots are the points where the head was known. The scale unit is metres. Please note that for this first step, the model has only 2 layers, with an homogeneous hydraulic conductivity for both of the layers. The recharge value is a mean value for the year.

Figure 5.1 Constant head modelling for February 5th, 2002.
The first piezometric map can be compared with the ones obtained during a previous study of the area (see Appendix C). For this previous study, three piezometric maps were modelled, by hand (interpolation based on the use of triangle method), with Microsoft Excel (simulation of the water table using an iterative process) and with SADA (Spatial Analysis and Decision Assistance) software (using ordinary kriging interpolation) (refer to FRTR, 2005, for more information about SADA). It appears that the four maps show some satisfying similarities, which might prove the reliability of the interpolation methods that were used, and especially of the GMS modelling.

This first step of modelling is quite satisfying since it is realistic and the general trend corresponds to what was expected. The flow is mainly from the East Side of the site to the river. Nevertheless, it can be noticed that on the northern, the eastern and the southern boundaries, heads lines are perpendicular to the bounds, which means that the flow is parallel to the bounds. As explained before, this comes from the fact that the grid is too small and the modelling boundaries are too close to the property boundaries of the site. The software is not able to compute the flow beyond the boundaries. Thus, the modelling has been run considering that no flow was crossing the boundaries.

For the annual head variation, results are similar except that several piezometric maps are presented with time intervals that have been chosen and entered in the model. For a one year simulation, it has been chosen to plot a map every 30 days, i.e. more or less for each month.
The graph in Figure 5.3 shows the evolution of the head for a point situated in the middle of the site. The modelling was run from January 1st and during 360 days (12 stress periods of 30 days). Thus, the first value on the curve (30 days), corresponds to the end of January and the last value (360 days) corresponds to the end of December.

![Figure 5.3  Annual head variation.](image)

On this chart, it appears that the groundwater level is maximum at the end of January and is minimum at the end of September. What is surprising is that the general trend of the annual head is opposite to the general trend of annual rainfalls (see Figure 4.3). This can be explained by the fact that rainfalls data are from 2004, while groundwater level data for September is from 2002 (24th). Now, on the particular year 2004, rainfalls were exceptionally high in August and September while it is usually the drier period in Göteborg. Consequently, since groundwater head data for September is from 2002, and given that rainfalls were low in this period, groundwater level was also low in September 2002. Therefore, even if trends are contradictory, this annual head variation is satisfying since it corresponds to the general trend of annual rainfalls in Göteborg, and more generally in southern Sweden, see e.g. Svensson (1984).

As explained before, even if this first modelling appears to be quite realistic, some improvements can be made: increasing the number of grid layers to have a more accurate representation of the site geology, generating an heterogeneous hydraulic conductivity to get a better representation of the filling material heterogeneity, and using transient data for precipitation to get a more accurate influence of the recharge.

Nevertheless, even if it is improved, no quantitative validation of the model can be done due to the lack of data. Indeed, a way to check the validity of the flow modelling would be to get rid of one of the points where the head was measured, and to verify if what is predicted by the model corresponds to the measured value of the head. Unfortunately, too few measurement points, and thus too few data, are available to afford to get rid of one point. However, the model could be qualitatively validated by comparing it with the ones that were obtained during the previous study carried out in 2004, as described before. Not only the four piezometric maps show some satisfying similarities, but also GMS modelling appears to be the more reliable since it is the one that takes into account the more characteristics of the soil and flow conditions.
5.1.2 Transport modelling

The first transport modelling was run with constant head (November 29th, 2004 data). Thus, the obtained results represent how contaminants spread over the field if the groundwater level was constant. Figure 5.4 and Figure 5.5 show the transport modelling for zinc after 1 day and after 3000 days.

![Zinc transport modelling after 1 day.](image)

It clearly appears that this modelling is not realistic at all. It is obvious that the contamination of the field cannot be only on scattered points but should be much more spread. The contaminated spots actually correspond to the sample points, and the starting concentrations for the rest of the site have been assigned to 0 mg.l\(^{-1}\), which does not coincide with the reality. That is why interpolating the starting concentration before running the transport modelling is so essential.

Visibly, on this simulation, diffusion appears to be the main process, while advection seems to be insignificant. This was rather expected since there is no groundwater flow, thus no movement, due to the fact that a constant head had been imposed. Nevertheless, what might be surprising is that from the polluted points, the contamination spreads quite homogeneously in every direction (isotropic spreading), without being influenced by the hydraulic gradient. Given that the hydraulic gradient is quite important, especially close to the river, it was rather expected that the contamination would spread faster in the river direction (i.e. in the decreasing hydraulic gradient direction) than in the others. This is something that will have to be checked with the improvement of the modelling.
5.1.3 4-layer modelling

The first improvement that has been carried out to the modelling was to increase the number of grid layers to get a better representation of the soil distribution. The 4-layer model has been run and compared to the 2-layer model, as shown in Figure 5.6.

Figure 5.5  Zinc transport modelling after 3000 days.

Figure 5.6  Comparison between the 2-layer flow modelling (left) and the 4-layer flow modelling (right) after 30 days.
Some slight differences can be noticed between the two models. Generally speaking, groundwater level is noticeably higher for the 4-layer modelling than for the 2-layer modelling. This is can be explained the fact that in the 4-layer modelling, the filling material layer is thinner, and thus the level of the clay is higher. Since clay has a very low hydraulic conductivity, it is almost impermeable and groundwater cannot flow through it. Thus, groundwater is restrained to flow in a thinner layer of soil. As an offset to the loss of flow volume in depth, groundwater gets this volume back in altitude, rising the groundwater table.

The 4-layer modelling will be adopted for the next simulations.

5.1.4 Interpolation of the starting concentrations

In order to avoid scattered contaminated points and problems of immediate pollutant dilution, interpolation of the concentration data has been performed, using ordinary kriging interpolation as explained before. Figure 5.7 shows the result of the ordinary kriging interpolation for zinc.

![Interpolation of zinc concentration data (2004 data).](image)

Light blue crosses mark out the position of the scattered points with known concentration that have been interpolated. The result of the interpolation has been
used as starting concentrations for the transport modelling. After 3600 days, zinc contamination has been computed to be spread as shown in Figure 5.8.

Figure 5.8 Zinc transport modelling after 3600 days.

Analysing the evolution of the contaminant plume on 3600 days, it appears that, contrary to the transport modelling without interpolation, the main transport process seems to be advection. The influence of groundwater flow on pollution is much more important than dispersion. This is all the more true as the hydraulic gradient is rather significant close to the river. Nevertheless, sorption also seems to have an important influence on pollution since pollutant transport is very slow (a few metres in almost 10 years).

Once more, even if the model appears to be quite realistic, no quantitative validation could be done, still because of the lack of data. A way to validate the model would be to run it for a first set of data, and to check if the contaminant concentrations that are predicted by the model correspond to a second set of data (few months later than the first set of data for example). Unfortunately, only one set of concentration data is available (for November 2004), and thus the model cannot be quantitatively validated.
5.1.5 Transient recharge

In order to improve the accuracy of the modelling, variation of recharge has been taken into account. Available data are not exactly the ones for the Wockatz site, but they are accurate enough to check the influence of rainfalls yearly variation on groundwater level. On the graph in Figure 5.9, the annual head variation have been plotted for a point situated in the middle of the site, both with constant and transient recharge. In that way, it is easy to check the influence of the variation of recharge.

![Figure 5.9](image)

*Figure 5.9  Annual head variation with constant recharge (in black) and with transient recharge (in red).*

On this chart, one can notice that the influence of recharge on the flow modelling is very light. Assigning transient recharge instead of constant recharge barely modifies the annual groundwater level variation results. Indeed, specified head data have a much more significant influence on the groundwater head annual variation than recharge data. For this reason, it is not necessary to get recharge data more adapted to Wockatz site, because the difference with Lejonet data might not be significant enough to be noticeable on the transport modelling.

5.1.6 Large grid modelling

Problems with boundary conditions could be observed with a small grid where the limits coincide with the property boundaries. Those problems could be avoided with the use of a larger grid as described before. A comparison between small grid and large grid flow modelling is presented in Figure 5.10 and Figure 5.11.
Figure 5.10  Small grid flow modelling after 30 days.

Figure 5.11  Large grid flow modelling after 30 days.
It can be noticed that there is no more problem at the level of the site boundaries: head lines are no more perpendicular to the boundaries, groundwater flows through the site boundaries. Groundwater head outside the Wockatz site must not be taken into account since no data were entered for this part and thus results are not accurate. The only purpose of increasing the grid size was to solve boundary conditions problems, not to extrapolate groundwater level.

Figure 5.12 and Figure 5.13 are a comparison between small grid and large grid modelling for zinc transport modelling after 3600 days.

**Figure 5.12** Small grid transport modelling for zinc after 3600 days.
Differences between small and large grid transport modelling are very slight. This can be explained by the fact that close to the site boundaries, contamination is quite low. Thus, since pollutant transport is very slow, the modification in groundwater head due to the increase of the grid is not significant enough to be noticeable in the transport modelling. Moreover, close to the boundaries where pollution is the highest (in the top right hand and in the bottom right hand corners), the hydraulic gradient is quite low. Therefore, advection is not the main transport process in these areas. Consequently, the slight modification in groundwater head due to the increase of the grid has almost no effect on pollutant transport.

5.1.7 Heterogeneous hydraulic conductivity

As expected, assigning a heterogeneous hydraulic conductivity in order to get a better representation of the filling material has a quite strong influence on the groundwater flow modelling, as shown in Figure 5.14.
Even if the heterogeneous $K$ model has only 2 layers, groundwater level tends to be higher with this model than with the homogeneous $K$. Moreover, head variation is noticeably different as shown on the charts in Figure 5.15 which represent the annual head variation for a point situated in the middle of the site.

Figure 5.14 Comparison between homogeneous $K$ 4-layer flow modelling (left) and heterogeneous $K$ 2-layer flow modelling (right) after 30 days.

Figure 5.15 Annual head variation for the homogeneous $K$ 4-layer flow modelling (top) and heterogeneous $K$ 2-layer flow modelling (bottom).
Nevertheless, even if groundwater flow modelling is quite different between the two models, the influence in the transport modelling is barely perceptible, as it can be noticed in Figure 5.16.

![Figure 5.16 Comparison between homogeneous K 4-layer transport modelling (left) and heterogeneous K 2-layer transport modelling (right) for zinc after 3600 days.](image)

The difference between the two models is small and not even visible. The fact that, despite an appreciable difference between flow modellings, transport modelling are very similar, which indicates the importance of the sorption process (retardation). Indeed, if advection was the main process, transport modelling would be much more affected by such a difference in the flow modelling. However, due to the predominance of the sorption process, the influence of groundwater flow on contaminant transport is highly reduced.

Because of the vagueness that makes the heterogeneous K model quite uncertain, results from the previous model will be analysed, i.e. from the 4-layer, large grid modelling.

### 5.2 Making the most of the results

Finally, according to modelling, 3600 days after the replacement of the upper part of the filling material, contamination by the four studied pollutants in Wockatz site should be as shown in Figure 5.17, Figure 5.18, Figure 5.19 and Figure 5.20.
Figure 5.17  Transport modelling for cadmium after 3600 days.

Figure 5.18  Transport modelling for copper after 3600 days.
Figure 5.19  Transport modelling for lead after 3600 days.

Figure 5.20  Transport modelling for zinc after 3600 days
A great number of outputs can be viewed by editing data set values or text files. Among other data, the total mass of contaminant in the aquifer and the total mass of contaminant that is gained or lost in the model for each time step are available. It is then easy to calculate contaminant flux that is discharged in the river or the percentage of pollutant that is been lost after 3600 days.

Results confirm that contaminant transport is a very slow process, mainly due to sorption of pollutants in soil. In almost 10 years, the total mass of pollutants in aquifer has decreased by an average of 23% (24% for cadmium, 23% for copper, 23% for lead and 22% for zinc). Since the river is the only sink for groundwater, and thus for contaminants, the whole loss of contaminants from the field corresponds to the contaminant discharge to the river. The flux of contaminants flowing toward the river could easily be calculated by dividing the lost mass of contaminant by the time. The charts shown in Figure 5.21 were obtained.

![Graphs showing contaminant fluxes](image)

*Figure 5.21  Contaminants fluxes toward the river, according to time.*

The normalised contaminant fluxes are shown in Figure 5.22.
Figure 5.22  Normalised contaminant fluxes toward the river, according to time.

It can be noticed that contaminants fluxes are decreasing with time. This was expected since the total mass of pollutant is logically decreasing with time (there is no source of pollution in the modelling). Cadmium is the contaminant that decreases the fastest (24% in 3600 days). This can be explained by the fact that cadmium is the pollutant that has the lowest $K_d$ value. Thus, it is the most mobile pollutant. Zinc is the contaminant that decreases the slowest. That might come from the fact that it is also the contaminant with the highest concentration. Copper and lead fluxes have the same order of magnitude and the same evolution.
6 Short evaluation of the use of GMS for advanced numerical modelling of groundwater contaminant transport

GMS is a very powerful and extensive groundwater modelling software. It for building comprehensive and realistic models that cannot be achieved by hand. It is very well organised and quite clear. It offers a lot of options that are logically arranged. A short review of the software is given below.

Tutorials and help:

GMS tutorials are well explained and easy to follow. They are attractive and can be approached as a kind of game. Nevertheless, even if a lot of explanations accompany the different examples, sometimes some parameters or values are assigned without any explanation about what they represent. The different scenarios are just examples and they are usually not suitable for the studied situation. They have to be adapted, which is not always obvious due to the lack of information about the different parameters. However, GMS Help is available and very comprehensive. Every module, parameter and option is clearly detailed and explained. Thus it is possible to learn how to use and to master the software by oneself. GMS can be practised even without any experience of this kind of software.

Time it took to perform modelling:

When not familiar with the software, it takes quite a long time to build and run the first model, learning step by step how to enter all the necessary data in the right order. Usually, some problems occur because of an omitted step or parameter, and it might take some times before finding where the problem comes from. However, after a few trials, entering the data for the model becomes fast. Of course, the bigger the model is, the more time it takes to run it. The last modelling that were obtained for this project could be achieved in a few hours: about 1 hour to build the model and to enter the data, around 15 minutes to run MODFLOW, a few minutes to adjust the different parameters for the interpolation, around 15 minutes to run MT3DMS, and the same to save the modelling as a film loop.

Files size:

One of the constraints of GMS is that modellings are very space demanding. Indeed, more than 12 gigabytes were necessary for the whole project. The most complete modellings that have been realised in this case are around 900 megabits each. Even if it is not necessary to have a very powerful computer to run GMS, it is however necessary to vacate a lot of space on the hard disk.
Modelling outputs:

Besides the modelling outputs that were used and explained in the previous part, other outputs are available, such as cell by cell data set values (head or concentration), time step by time step. It is also possible to define some observation points wherever on the model, and to plot time series for these points. Many types of graphs such as error or residual can also be plotted versus different parameters. The great number of available outputs is a strong asset of the software.

How does the software meet expectations?:

Meeting expectations depends on the set objectives. In the present case, the purpose of the project was to set up a groundwater transport model for the Wockatz site in order to gain increased knowledge of the contaminant transport conditions at the site with special emphasis on the contaminant load on Göta älv. Results are satisfactory in the way that realistic groundwater flow modelling could be achieved, and that contaminant transport modelling could be performed in the most representative way, even with very limited data. Contaminant load in the area and contaminant discharge in the river could be estimated, which is what was expected from the model for the specific scenario where the upper layer of filling material would have been removed. Thus, it can be said that GMS brought a satisfactory answer to objectives that were set.

Encountered problems and shortages:

Nevertheless, some problems were encountered while using the software, and a lot of time was lost trying to solve them. One of the shortages of GMS is that not enough details are given about calculation failures. For instance, when the model is not converging, there is no detail about which cell is concerned and why. Thus, it is quite difficult and time consuming to calibrate and adapt the hydraulic conductivity (for example) in order to improve the model. This has to be done, running the model for dozens of time, which means a huge loss of time. It would be nice to know exactly what is wrong in the calculation in order to be able to go straight to the source of the problem and to correct it directly.

What did the software bring on top of usual calculations/estimations?:

The use of GMS provided a great source of progress for groundwater contaminant transport modelling, especially compared with the previous project that was carried out, for the Wockatz site. Indeed, for this project, approximate calculations were done, providing only rough orders of magnitude as results. The use of a numerical model allows to build a much more accurate and realistic modelling of the situation, even with few input data. Even if they might be slightly different from the reality, results are much more relevant when using a numerical model than an analytical model where lots of approximations and assumptions are usually necessary.
7 Conclusions

An interesting and satisfactory modelling of the Wockatz site could be achieved and used in order to predict contaminant spreading and to be able to remediate the site. This modelling is only valid for the specific scenario of a basic remedial action, i.e. if the upper part of the filling material has been removed and replaced by non contaminated soil with same hydraulics characteristics. The modelling indicates that the Wockatz site is heavily contaminated. Pollutants are distributed both in the soil and water media, and move with and within groundwater. However, according to transport modelling, it is a very slow process, and several decades would be necessary for the transport of the majority of the contaminants mass away from the site if nothing else than replacing the filling material is done. This means that in the current situation where nothing at all has been done to the site, it would take hundreds of years for the site not to be contaminated anymore. That is why it is obviously necessary to take some remedial actions, such as removing the whole layer of contaminated soil, and at the same time, because groundwater level is rather low, remediating the contaminated groundwater. Another action that would accelerate the site recovery would be to prevent recharge to groundwater (by covering the soil with an impermeable material for example). This would make the groundwater level decrease. Then, if necessary, a layer of clean material just has to be added on top of the impermeable material, to get the same type of soil as previously, but without any contact with contaminated soil or groundwater.

One of the weaknesses of the modelling is that, even if it appears to be realistic, especially for flow modelling, no quantitative validation of the modelling could be done, due to the lack of data. This is why it is necessary to carry out more investigations and sampling campaigns, in order to both build a more accurate model, and to check the validity of the model. More head data are required not only during the same year to get a more accurate annual variation model, but also on several years to check if the variation is more or less the same every year. It is obviously necessary to get more concentration data: more scattered sampling spots are required in order to have a better representation of the whole area, and for these points, regular samplings should be done and analysed in order to be able to visualise the true transport pattern of the contamination. Finally, it would be interesting to get more geological data, so that an observed soil distribution could be used instead of assumptions and unconditional material set generation. No data were available regarding the soil. Soil distribution and characteristics were assumed, based on typical values. Those parameters might have a significant influence on flow modelling, and thus some soil samplings should be carried out. If no data can be obtained concerning the geology of the site, the heterogeneous hydraulic conductivity modelling should be pursued since it is supposed to be the one with the better representation of the soil. The time frame of this project and the lack of input data did not allow to investigate this modelling as much as it could be, but it provide a good basis for further studies.

GMS has proven to be a useful and efficient tool in the investigation of the contaminated Wockatz site. Relevant results could be obtained from the models and confirm that numerical groundwater modellings are much more effective and pertinent for groundwater transport predictions than analytical calculations.
8 References


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9 Appendices

Appendix A: Map of Sweden with localisation of Göteborg
Appendix B: Map of Göteborg with localisation of the Wockatz site
Appendix C: Piezometric maps of groundwater in the Wockatz area
Appendix A: Map of Sweden with localisation of Göteborg
Appendix B: Map of Göteborg with localisation of the Wockatz site
Appendix C: Piezometric maps of groundwater in the Wockatz area

Map 1: modelling by hand
Map 2: modelling with Excel

Map 3: modelling with SADA (ordinary kriging interpolation)