Hydrogeological Modeling to Improve Remediation Strategies for a Drinking Water Aquifer Contaminated by an Aqueous Phase Liquid

Martin Bergvall
Faculty of Forest Sciences
Department of Forest Ecology and Management
Umeå

Doctoral Thesis
Swedish University of Agricultural Sciences
Umeå 2011

Acta Universitatis agriculturae Sueciae
2011:26

Cover: Simulated contamination plume of 2,6-dichlorobenzoamide (BAM) in the groundwater flowing from the former nursery in Piparböle, viewed from above at an oblique angle.

ISSN 1652-6880
ISBN 978-91-576-7561-3

Print: Arkitektkopia, Umeå 2011

Hydrogeological Modeling to Improve Remediation Strategies for a Drinking Water Aquifer Contaminated by an Aqueous Phase Liquid

Abstract

In many communities, groundwater is an important source of drinking water. Groundwater aquifers are, however, vulnerable to the widespread and increasing problem of contamination from anthropogenic sources. Once in the groundwater, contaminants are likely to remain there for a long time as the attenuation rate is slow. In this thesis, different tools for modeling subsurface transport were adapted and evaluated in order to improve remediation strategies for a contaminated esker aquifer. The work focuses on the entire transport process at a regional scale from the source at the soil surface, through the vadose zone, and in groundwater. Few comparable studies exist, especially for aquifer systems in glaciofluvial sediments. The studied aquifer supplies drinking water to the municipality of Umeå, which is a medium-sized city in northern Sweden. The aquifer is contaminated by the commonly found pesticide degradation product 2,6-dichlorobenzoamide (BAM). Hydrogeological and chemical field data were collected, and the contaminant migration analyzed by a stationary non-distributed model and a transient distributed model. To remediate the aquifer so that it meets the drinking water standard, it was necessary to combine extraction at two up-gradient wells, with an increased rate of artificial recharge via two infiltration ponds. Using only one of the techniques would either affect the water balance negatively, or would increase the risk of clogging the infiltrating surface. However, in order to reinstate the two up-gradient wells as producers of drinking water as soon as possible, it was necessary to establish the remediation wells in close proximity to the contaminant source. When the data quality is insufficient the simple mass-balance model was found to be most useful, since it reflects the uncertainty of the result. However, if it is essential for the contaminant transport to be calculated more accurately, a distributed model is required. To strengthen the credibility of such a model, it should be validated with independent data from various sources: in this study it was stable isotope oxygen-18 data, data on the BAM contamination, and time-variant hydraulic head data. The overall findings are expected to be relevant to many other sites in similar settings.

Keywords: dichlobenil, distributed model, esker, glaciofluvial, groundwater, mass-balance model, pesticide, subsurface, vadose zone

Author's address: Martin Bergvall, SLU, Department of Forest Ecology and Management, 901 83 Umeå, Sweden
E-mail: martin.bergvall@tyrens.se

Dedication

To Hanna, Maj and Signe

Groundwater flows slowly…

Contents

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I Bergvall, M., Grip H., Sjöström, J. and Laudon, H. (2004). Contaminant transport in a municipal drinking water supply: a steady-state approach to estimate rate and uncertainty. *Ambio* 36(6), 512-519.

II Larsson*, M. and Grip H. (2004). Local scale modeling of dichlobenil movement through a sandy soil by the finite element model HYDRUS-1D. *In: Kovar, K., et al. (Eds.) Proceedings of Finite Element Models, MODFLOW, and More: Solving Groundwater Problems, Karlovy Vary, Czech Republic*, pp 211-214.

III Bergvall, M., Grip H., Sjöström, J. and Laudon, H. (2011). Modeling subsurface transport in extensive glaciofluvial and littoral sediments to remediate a municipal drinking water aquifer. *Hydrology and Earth System Sciences Discussion* 8(1), 1729-1764. Changed according to reviewer comments in order to resubmit to *Hydrology and Earth System Sciences*.

IV Bergvall, M., Grip H. and Laudon, H. (2011). The use of oxygen-18 and numerical modeling to optimize the management of a contaminated groundwater resource (submitted manuscript).

*) Former last name was Larsson (paper II), presently it is Bergvall (paper I, III, and IV).

The contribution of Martin Bergvall to the papers included in this thesis amounted to about 90-95 % of the total work load, including field surveys, sampling, soil physical analyses, computer modeling, literature review and scientific writing. Measurements of groundwater levels, soil characteristics, and other information used in the thesis carried out prior to 2003, has been collected and documented by workers at the municipality. Chemical analyses and isotopic information has been analyzed by external laboratories. At an early stage of this study the supervisors Laudon, Grip and Sjöström helped to plan and design the investigation and have later in the process reviewed and commented several versions of the manuscripts.

1 Introduction

1.1 Contamination of drinking water aquifers

Groundwater is a valuable supply of drinking water in many societies. However, throughout the world, an increasing number of aquifers are being contaminated by chemicals from anthropogenic sources. Pesticides and their degradation products are among the most commonly reported contaminants in Europe (Pavlis *et al.*, 2010; Leistra & Boesten, 1989) and the US (Barbash *et al.*, 2001; Kolpin *et al.*, 1998). In Sweden there are about 1900 municipal drinking water plants that draw their supplies from natural or artificial groundwater. During a national monitoring program, about 30 % of the groundwater supplies investigated between 2005 and 2009 were noted to be contaminated with pesticides (CKB, 2009; Törnquist *et al.*, 2007), at levels that exceed both the Swedish and the European standards (0.1μg l^{-1}) for drinking water quality (EU, 2006). Similar levels of contamination have been reported in many countries (Pukkila *et al.*, 2009; Morvan *et al.*, 2006; Clausen *et al.*, 2004; Versteegh & te Biesebeek, 2003; Wolter *et al.*, 2001). In Sweden, BAM (2,6-dichlorobenzoamide) has been found to be the most common contaminant, reported in 60 % of the contaminated groundwater supplies. BAM is a hydrophilic degradation product of the herbicide dichlobenil (2,6-dichlorobenzonitrile) and is highly persistent in soil (Cox, 1997).

The greatest concern regarding human exposure to pesticides is their presence in water (Younes & Galal-Gorchev, 2000). Decades may have passed since the use of some of these substances ceased, but they can continue to leach from soils to groundwater due to their low degradation rates and sorption to fine soil particles, organic matter, and minerals. Once

in the groundwater, pesticides and their degradation products are likely to remain there as the attenuation rate is slow (Pavlis *et al.*, 2010).

1.2 Evaluation and measures of contaminated sites

In general, potentially contaminated sites are identified and classified with risk assessments. Although methods of analyzing risks associated with contaminated soils vary among countries, generic guidelines have been developed by the various environmental authorities (Crommentuijn *et al.*, 2000a; Crommentuijn *et al.*, 2000b; CCME, 1996; SEPA, 1996; USEPA, 1996). These guidelines indicate contaminant concentrations that may lead to undesirable effects on human health or the environment. If a site is classified as being a 'high' or 'very high' risk, further investigations are necessary. In soil and groundwater, such classifications often presuppose suitable conditions for dispersal, which is the common status of groundwater aquifers supplying drinking water. Risk classifications are, however, often based on rough estimates and can therefore be uncertain. For example, due to heterogeneous geology the actual rate of contaminant movement in soil and groundwater can vary from its estimated rate by several orders of magnitude.

For the remediation of contaminated sites there are two main strategies: i) to hinder, modify or remove the migration of the contaminant from the source to the environment (Albergaria *et al.*, 2006; Chang & Yen, 2006; Rugner *et al.*, 2006; Seol *et al.*, 2003); or ii) to protect the recipients from contamination by filters, barriers or pumping (Chang *et al.*, 2010; Thiruverikatachari *et al.*, 2008; Chang *et al.*, 2007). New techniques are continuously being developed to manipulate the contaminant source, but the latter strategy may be necessary for non-point sources as well as for contaminant plumes that have migrated long distances in the subsurface. When groundwater is used as a supply of drinking water, the management of an artificial aquifer recharge has also proven to be successful in meeting the standards for drinking water quality (Szucs *et al.*, 2009; Hiscock & Grischek, 2002). However, because of the heterogeneous conditions of the subsurface and the contaminants' adherence to soil particles, there are arguments that once an aquifer has been contaminated it is difficult, if not impossible, to restore it to its original state (Travis & Doty, 1990).

1.3 Modeling approaches

The large number of contaminated groundwater supplies highlights the need for tools to evaluate the subsurface processes controlling contaminant transport. In the evaluation of contaminated sites it is not uncommon that the depth of the vadose zone is not specifically represented, and that the permeability of the whole aquifer is represented by a single hydraulic conductivity value (SEPA, 1996). In order to improve the evaluation and prediction of contaminant movement, and provide decision support for remediation strategies, it is essential that contaminant transport is calculated in more detail. Specifically, it is crucial that the transit time from the source to sensitive recipients is determined more precisely, and that the concentration of contaminant by the time it reaches the recipients is predicted more accurately.

Because the governing equations for subsurface flow and mass transport are partial differential equations (PDE), it is necessary to define appropriate boundary conditions. A direct analytical solution is only possible for domains of simple geometric shape or for homogeneous media (Strack, 1999). Instead of trying to solve the PDE, one alternative option is to use a simple non-distributed mass-balance approach, based on the contaminant mass and the water balance, to calculate the dilution of contaminant leakage into the aquifer (USEPA, 1996). However, the usual method is to use a distributed model, in which the study area is subdivided into small, finite, calculation cells, and to replace the PDE by approximate, algebraic functions. The main numerical approaches used in practice are the finite-difference method (FDM) and the finite-element method (FEM). However, FEM has not been used frequently in earlier groundwater modeling exercises, probably because it is more demanding of computing power.

Subsurface water flow is normally independent of the contaminant being transported. The exception is when the concentration of contaminants affects the water density and hence the water flow. For water soluble, moderately concentrated contaminants, this means that there is no requirement to solve the flow and transport equations simultaneously (Domenico & Schwartz, 1998). Therefore, a common model approach is first to calculate the velocity field, and second to calculate the mass transport (Fig. 1). This approach also has the advantage that it can generate stable, converging solutions of the flow field, and that it is possible to include more sophisticated geochemical models.

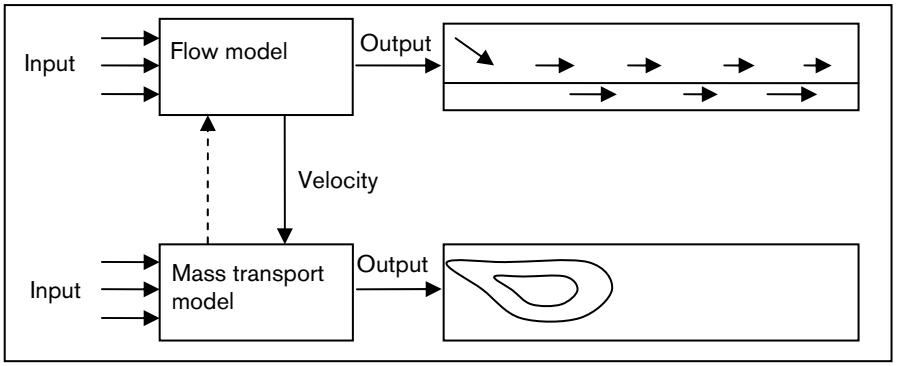

Figure 1. The usual relationship between flow and mass transport models in simulating the distribution of contaminants.

Groundwater flow is a simplified case of flow in the vadose zone. It is therefore common to use different modeling approaches, each optimized for each of the zones. Several authors have proposed coupled models for transport in the vadose and groundwater zones (Weill *et al.*, 2009; Panday & Huyakorn, 2008; Twarakavi *et al.*, 2008; Herbst *et al.*, 2005), but models also exist that operate for both zones simultaneously (Hughes & Liu, 2008; Trefry & Muffels, 2007).

In general, distributed numerical models vary in complexity and the most comprehensive ones take into account the heterogeneity of the modeled environment. Their practical application is, however, often hindered because there is insufficient data that justify their complexity (Hantush *et al.*, 2000). Nevertheless, at specific sites with adequate field data, it is often appropriate to perform more detailed calculations through simulations in a distributed numerical model (Prommer *et al.*, 2000). Other options include Monte Carlo simulations based on parameter distribution functions (Soutter & Musy, 1998), the closely related fuzzy-set theory (Zhang *et al.*, 2009; Li *et al.*, 2007), and other methods that have been suggested as being more specifically capable of handling prediction uncertainty (Li *et al.*, 2003; Wong & Yeh, 2002).

Depending on the extent to which a site-specific model has been validated, it can be used to predict the behavior of contaminants over reasonably long time-scales and under a variety of conditions (Hassan, 2004). To support the model validation it is necessary to have independent data. Since there are an infinite number of non-unique solutions to the groundwater flow and transport problem at the starting point, it is beneficial to be able to use a range of different types of data for validation purposes. Commonly used validation data include hydraulic heads and flow data, although other types of input may also be used – for example contamination

data, temperature, and isotopes such as those pertaining to the stable isotopes hydrogen-2 (deuterium) and oxygen-18 in water. However, there are only few examples in the literature where stable isotope data have been used to validate groundwater-flow models (Stichler *et al.*, 2008; Hunt *et al.*, 2005; Krabbenhoft *et al.*, 1990). Still fewer of these models have also been validated with data on groundwater contamination. Nevertheless, the combination of independent data types would improve the site-specific knowledge of flows and contaminant movements.

Many studies have related hydrogeological models to the remediation of contaminated sites. Several authors have either considered contaminant transport in groundwater at a regional scale (Szucs *et al.*, 2009; Maqsood *et al.*, 2005; Zhou *et al.*, 2004; Schäfer & Therrien, 1995) or if both the vadose and groundwater zones have been included (Stenemo *et al.*, 2005; Jorgensen *et al.*, 2004), the studies have been carried out at a local scale. Few studies have been performed at a regional scale that cover the entire transport process from contamination at the soil surface, through subsurface transport, to the planning of remediation strategies. Still fewer studies have modeled the subsurface transport processes in glaciofluvial esker aquifers, which are generally extensive in both depth and range. Those existing studies have commonly only considered the groundwater zone (Eyles & Meriano, 2010; Sudicky *et al.*, 2010; Ross *et al.*, 2005; Artimo, 2002). The lack of models for eskers at this scale is problematic since many of the most important groundwater resources in recently glaciated regions of the world are situated in such settings.

The numerical problem for predicting contaminant transport in the vadose zone and in groundwater often becomes extremely demanding of computational power. A review of the literature shows that there has been an increasing tendency for the numerical problems to be solved on networks of computers, which are not publically available. One example is a study on the effectiveness of aquifer remediation (Maxwell *et al.*, 2008), in which the numerical problem was solved on a network of 200 processors. Another fact that emerges from the literature is that synthetic examples dominate and, if field sites with real data are considered, the use of hypothetical contaminants is common (Maji & Sudicky, 2008; Maxwell *et al.*, 2008; Rauber *et al.*, 1998). Many studies function merely as demonstrators for specific numerical methods, simulators, or various remediation techniques. An important research challenge is therefore to focus more broadly on integrating appropriate methodological developments with the realities of field observations at specific sites to help solve real problems of the subsurface environment (Gelhar, 1997).

1.4 Objective

The objective of the work presented in this thesis was to adapt and evaluate different modeling tools for subsurface transport using empirical hydrogeological and chemical field data collected from a contaminated site, and to use the results to plan remediation strategies. For its general usefulness, there was a requirement that any model should be capable of being run on a standard personal computer. To this end, different tools were applied to model the contamination by an aqueous phase liquid, of the groundwater aquifer supplying the municipal drinking water utility in Umeå, which is a city in northern Sweden with a population of 115 000.

2 Materials and methods

2.1 Subsurface flow and transport processes

2.1.1 Vadose zone

Subsurface flow at a certain head gradient is determined by the density, viscosity and compressibility of the liquid, and by the water content, permeability and compressibility of the porous media. If water is assumed to be the only liquid and incompressible, which implies constant density, we get an equation, often referred to as the Richards equation, which relates transient flow and water content. For simplicity, only vertical flow is assumed:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\psi)\left(\frac{\partial \psi}{\partial z} + 1 \right) \right] - q_s , \qquad \text{(Eq. 1)}$$

where θ is the volumetric water content; t is time; z is the spatial coordinate (positive upward); K is the unsaturated hydraulic conductivity; ψ is the pressure head; and q_s is a sink term.

Flow in the vadose zone is driven by gravity and the three-dimensional gradient of soil-water potential. Surface runoff may occur, depending on the structure, texture and slope of the soil surface. If there are tilting layers with different hydraulic conductivities under the soil surface, lateral flow in the vadose zone may also occur.

Various empirical methods exist to describe the relation between water content, pressure head and unsaturated hydraulic conductivity. The van Genuchten-Mualem model is one of the most frequently used (van Genuchten, 1980):

$$\begin{cases} \theta(\psi) = \begin{cases} \theta_r + \dfrac{\theta_s - \theta_r}{\left(1 + |\alpha\psi|^N\right)^M} & h < 0 \\ \theta_s & h \geq 0 \end{cases} \\ K(\psi) = K_s S_e^{1/2}\left[1 - \left(1 - S_e^{1/M}\right)^M\right]^2 \\ \text{where} \\ S_e = \left(1 + |\alpha\psi|^N\right)^{-M} \\ M = 1 - \dfrac{1}{N} \end{cases}, \qquad \text{(Eq. 2)}$$

where α and N are empirical parameters describing the characteristic pore size and the tortuousness of the soil matrix, respectively; K_s and θ_s is the saturated hydraulic conductivity and water content, respectively; and θ_r is the residual water content.

A requirement for Eqs. 1 and 2 is that the soil matrix must be represented by a continuum, which has replaced all pores and particles. However, flow at the micro scale is important for contaminant transport and the process refers to mechanical dispersion. Another process with similar effect is molecular diffusion, in which transport is caused by concentration gradients. Molecular diffusion is important at low flow velocities. Together, these two processes represent hydrodynamic dispersion, which has a corresponding importance for contaminant transport, as does hydraulic conductivity for flow. In the one-dimensional case, the so-called advection-dispersion equation is:

$$\frac{\partial(c\theta)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial\left(c\theta v_z\right)}{\partial z}, \qquad \text{(Eq. 3)}$$

where c is the contaminant concentration; D is the effective hydrodynamic dispersion coefficient; and v_z is the flow velocity.

The mobility of contaminants is also affected by sorption to organic matter, clay colloids, and minerals. If sorption is added to Eq. 3 it becomes:

$$\frac{\partial(c\theta + \rho_b S)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial\left(c\theta v_z\right)}{\partial z}, \qquad \text{(Eq. 4)}$$

where ρ_b is the bulk density, and S is the quantity of mass sorbed onto soil particles.

Sorption can be described in various ways by linear as well as non-linear models. Assuming chemical equilibrium a generalized form of the adsorption isotherm is:

$$S = \frac{K_d c^{\beta}}{1 + \eta c^{\beta}}, \qquad \text{(Eq. 5)}$$

where K_d is the partitioning coefficient of sorbed to solution contaminant concentration; and β and η are empirical coefficients to describe the sorption capacity.

When β = 1 Eq. 5 transforms to the Langmuir isotherm, which behaves linearly at low concentrations but approaches a constant value at high concentrations. When η = 0 it transforms to the Freundlich isotherm, which becomes linear if β = 1. Sorption of organic compounds is commonly related to the amount of organic carbon:

$$K_d = K_{oc} f_{oc}, \qquad \text{(Eq. 6)}$$

where K_{oc} is the sorption coefficient of soil organic carbon and f_{oc} is the weight fraction of organic carbon.

To consider sources and sinks Eq. 4 expands to:

$$\frac{\partial(c\theta + \rho_b S)}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial\left(c\theta v_z\right)}{\partial z} + \sum_k Z_k, \qquad \text{(Eq. 7)}$$

where Z_k represents all kinds of mass sources and sinks.

Important sinks are vaporization, acid-base reactions, redox reactions, cation exchange, and microbiologically mediated reactions. Saripalli *et al.* (2001) present an overview of how various chemical reactions may affect hydrogeological properties.

The simplest way to describe degradation is through the first-order kinetics, which is frequently applied to radioactive decay and the microbiological degradation of organic substances:

$$\frac{\partial c}{\partial t} = -\mu c, \qquad \text{(Eq. 8)}$$

where μ is a first-order rate constant.

Contaminant transport is also influenced by diffusion from dead-end pores holding immobile water. That is, the effective water content that

conducts the contaminant is less than the volumetric water content of the soil, θ. This means that a breakthrough of the contaminant concentration fades later than might otherwise be expected from the advection-dispersion equation (Eq. 3). Equation 3 can, however, be adjusted by partitioning the water into mobile and immobile phases.

Another process is the formation of macropores by plant roots, animal burrows, shrinkage fissures, heavy rainfall, or by the erosive action of subsurface flows. Depending on the texture and structure of the soil, macropores may persist between wetting periods. The macropores may cause preferential flow, which is a fast flow that does not conform to those common soil hydraulic properties described in Eq. 2. The importance of preferential flow is determined by the texture and structure of the soil. Sandy soils are often considered the most vulnerable to contaminant leaching because of their high saturated hydraulic conductivity. However, sandy soils are unstructured, which means that macropores are unstable, and that matrix flow dominates. More fine-grained soils, such as silt, clay and till soils, have lower saturated hydraulic conductivity values, but they are structured and have a high tendency for flow to occur in macropores (Kordel *et al.*, 2008). Structured soils are likely to generate higher peaks of contaminant losses because of preferential flow (Brown *et al.*, 2000). Since matrix flow is dominant in sandy soils, the breakthrough curve becomes broader, indicating that contamination can feed into groundwater over very long periods. Thus, even if the peak concentrations from the vadose zone are reduced in sandy soils, the exposure time to groundwater is expected to be long. This stresses the need for adopting different approaches when dealing with soils with diverse properties.

2.1.2 Groundwater

In groundwater, Eq. 1 is simplified because saturation is 100 %. In three dimensions it turns into:

$$S_s \frac{\partial h}{\partial t} = \frac{\partial}{\partial x}\left(K_x \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial h}{\partial z} \right) - q_s , \qquad \text{(Eq. 9)}$$

where S_s is the specific storativity. In stationary models the left-hand side of Eq. 9 equals zero.

The advection-dispersion equation (Eq. 3) remains the same except that the dispersion term becomes unaffected by the water content, which is constant. The water content in groundwater that affects transport can be referred to as the kinematic porosity or effective porosity, which is less than the total porosity. To consider sorption, and sources and sinks of

contaminants in groundwater, the one-dimensional equation, corresponding to Eq. (7), is:

$$\frac{\partial(cp_k + \rho_b S)}{\partial t} = \frac{\partial}{\partial x}\left(p_k D \frac{\partial c}{\partial x} \right) - \frac{\partial(cp_k v_x)}{\partial x} + \sum R_n \,, \qquad \text{(Eq. 10)}$$

where p_k is the kinematic porosity and R_n represents all kinds of mass sources and sinks. Important sinks in groundwater are acid-base reactions, dissolution of salts, redox reactions, cation exchange and pumping rates at extraction wells.

2.2 Site description and sampling

Initially, several contaminated sites in northern Sweden were evaluated in the search for a site where it would be possible to study a contaminant in field over a long time-period. A former tree nursery at Piparböle was identified as being the most suitable site. Pesticides had been used for a considerable time causing significant contamination, and the Piparböle site was classified as being a high level dispersal risk according to the Swedish methodology of surveying contaminated sites (SEPA, 2002). The site is located close to the drinking water aquifer of the municipality of Umeå, a medium-sized city in northern Sweden (Fig. 2). The use of the aquifer to supply drinking water explains why many investigations have been carried out in the area since the 1950s. Many of these studies had a hydrogeological, geological or geophysical focus, which provide useful data. The proximity of the site to the drinking water utility, supplying the majority of the 115 000 inhabitants in Umeå, also made the site interesting from a socio-economic point of view, although the latter aspect was not studied.

Piparböle was active as forest-plant nursery cultivating mainly spruce and pine seedlings between 1956 and 2002. At the main field, which covers 12 ha, several kinds of pesticides were used to kill unwanted weeds, vermin and fungi. Among the pesticides used, DDT and Totex are the most important. DDT applied during the 1960s to kill pine weevil has been found in the topsoil in concentrations exceeding 20 mg kg^{-1}. In 2003, this led to an excavation of approximately 0.2 m of the topsoil in the entire 12 ha area. Totex consists of equal amounts of dichlobenil and 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine (atrazine) and was used to kill unwanted weeds between the late 1970s until it was banned in 1991. Atrazine degrades to several compounds, many of which have been found in the groundwater. Dichlobenil degrades to the highly water-soluble substance

BAM (Fig. 3). Various chemical properties of dichlobenil, BAM, atrazine and DDT are summarized in Table 1.

Table 1. *Chemical properties of the pesticides dichlobenil, BAM (degradation product of dichlobenil), atrazine, and DDT, which had been used at the nursery. The water solubility, the sorption coefficient of soil organic carbon, K_{oc}, and the half-life of degradation, $T_{1/2}$, are taken from Hornsby et al. (1996).*

Substance	Solubility (mg l^{-1})	K_{oc} (l kg^{-1})	$T_{1/2}$ (days)
Dichlobenil	21	400	60
BAM	11000	33	660
Atrazine	33	100	60
DDT	0.0055	2000000	2000

In this study only dichlobenil and its degradation product, BAM, were considered since there is much concern regarding BAM due to its high mobility. The concentration of BAM has exceeded the European drinking water standard for pesticides (0.1 μg l^{-1}) in the two extraction wells at Kulla, and in six out of the twenty extraction wells located at Forslunda (Fig. 2). In the Kulla wells, groundwater measurements began in 1998 and, since then, BAM has been found at concentrations up to 22 times greater than the drinking water standard. In the six most easterly wells at Forslunda, BAM analyses started in 2005 and show that the standard have been exceeded by up to four times. The nursery situated in Piparböle has been identified as the source of the contamination.

Records from the nursery suggest that Totex was initially applied during the transition from growing bare-rooted seedlings on open land, to their production in small containers on open land. The transition between these production methods began during the 1970s and the records suggest that the first application of Totex occurred in 1976. Totex was mainly applied as a granular formulation along the length of plant beds, and at the short ends, where the irrigation system was located. The area over which the weed-killer was applied has been estimated from historical aerial photographs to be 4 % of the total nursery area. Since the soil has been repeatedly mixed over the years, it is probable that the remains of the herbicide have been spread over an even larger part of the area. According to the manufacturers of Totex, the recommended application rate would have varied between 0.16 and 1.7 g m^{-2}.

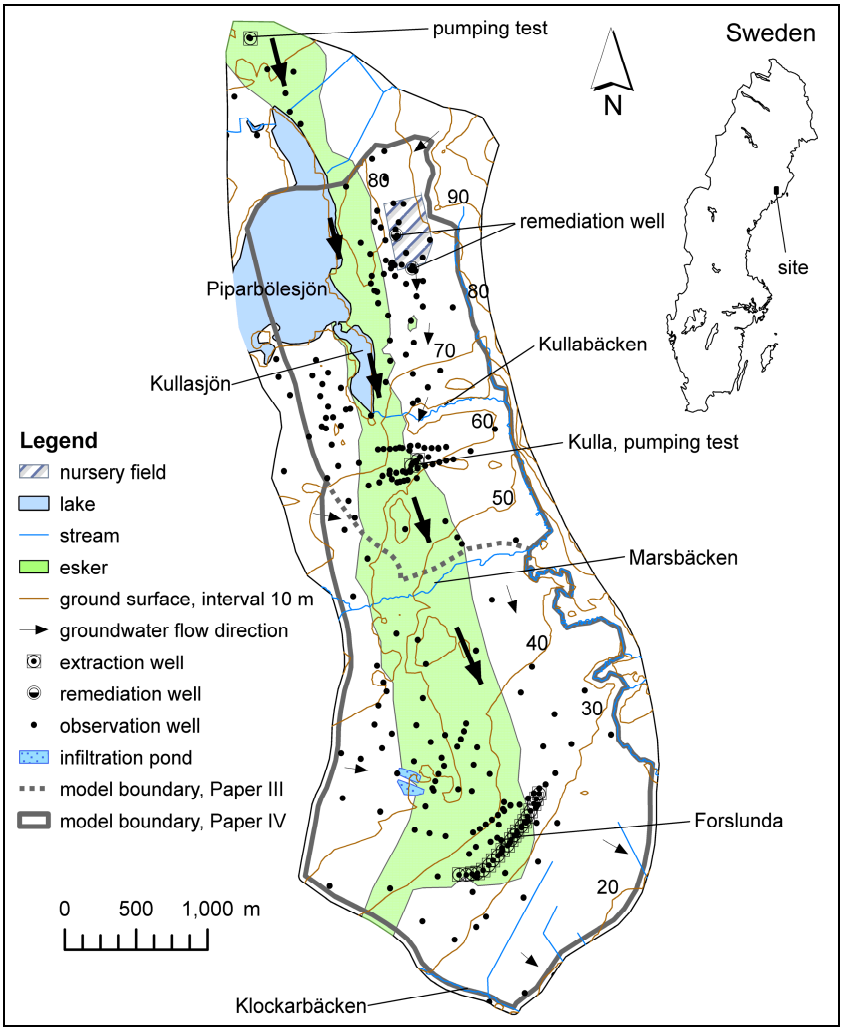

Figure 2. Location of the site within Sweden and map showing location of the nursery site (lat. 63°83'N, long. 20°26'E), extraction wells, remediation wells, observation wells, and boundaries of the distributed models. Arrows show the direction of groundwater flow, and visible are contour lines of the ground surface (20 m in the south), lakes, streams, the extent of esker material beneath the groundwater table, and infiltration ponds used for artificial recharge of the aquifer.

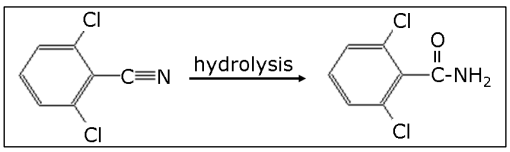

Figure 3. Structural formula of dichlobenil (2,6-dichlorobenzonitrile) with its degradation product BAM (2,6-dichlorobenzoamide). The hydrolysis is primarily a microbiologically mediated process.

The soil at the nursery is about 10 m deep and consists of well-sorted, littoral sand with almost no structure due to the coarse grain distribution. The general direction of groundwater movement from the nursery is southwards. Soil sampling of the vadose zone was performed in 2003 and 2009. The soil surface was screened for dichlobenil and BAM at six points at the site, from which samples were collected every 40 to 50 cm, down to a depth of 5 to 10 m. When analyzed, the samples showed that dichlobenil and BAM were spread over the total nursery area and that both compounds do move downwards. The concentrations of total organic carbon were low in the soil (mean 2.6 g kg^{-1}, standard deviation 1.2 g kg^{-1}) as well as in the pore water (mean 4.1 mg l^{-1}, standard deviation 0.8 mg l^{-1}). The analysis of soil texture showed that 70 to 94 % of the soil down to a depth of 1.7 m was classified as medium sand or coarser. At most, 21 % of the soil at a depth of 4.2 m was classified as medium silt or finer, 3 % of which was clay (Table 2). The soil water content was first analyzed by the oven-drying method, and then measured on several occasions with a depth moisture probe (Nucletronics Aps, Borre, Denmark) at every 0.2 m-depth (mean water content between 4.5 and 24.1 %, depending on depth).

The nearby esker Vindelälvsåsen, which consists of glaciofluvial sand and gravel, is partly covered by thin layers of silt and clay, especially along the sides. Layers of silt and clay also underlie the lakes Piparbölesjön and Kullasjön (Fig. 2), which causes the groundwater head at the southern end of Kullasjön to be 27 to 28 m below the surface water head. However, the esker is also partly located beneath the silty and clayey beds of the lakes. Kullasjön has an outlet in the south, which is the stream Kullabäcken. The latter together with the streams Marsbäcken and Klockarbäcken (Fig. 2), leak a significant amount of surface water to the underlying esker along parts of their courses. Tests with salt injections have estimated the mean leakage from Kullabäcken to be 11 l s^{-1}, which is 7 % of the mean discharge rate.

The two northerly extraction wells are located in an area where the esker is about 50 m deep and 600 m wide. The shape of the esker is less pronounced at the well chain where the esker is about half as deep but twice as wide. The esker contains large quantities of groundwater and provides the main part of the municipality's drinking water. However, the equivalent of about 60 % of the total volume of water extracted annually is infiltrated via two ponds. The surface water for infiltration is pumped from the nearby river Umeälven. In total the extraction wells supply the municipality's drinking water utility at an annual mean rate of 280 l s^{-1}. As a matter of interest, some events during the history of the municipality's water supply are summarized in Table 3.

Table 2. *Analyzed soil textures sampled at the nursery given as percentages by weight.*

Depth [m]	Fine gravel	Coarse sand	Medium sand	Fine sand	Coarse silt	Medium silt	Fine silt	Clay
	2-6 mm	0.6-2 mm	0.2-0.6 mm	0.06-0.2 mm	0.02-0.06 mm	0.006-0.02 mm	0.002-0.006 mm	<0.002 mm
0.1	1	16	73	8	2			
0.2	1	16	73	8	2			
0.3		39	55	5	1			
0.4	2	36	51	9	2			
0.5	2	21	59	16	2			
0.7	3	37	42	16	2			
0.9	4	23	43	28	2			
1.2	6	17	57	17	3			
1.7	1	10	60	26	3			
2.6			4	58	32	6		
3.3			5	54	31	7	3	
4.2			7	47	25	11	7	3
5.0			13	55	22	10		
6.2			2	54	24	13	5	2
7.0			8	71	16	5		
7.3			21	55	14	7	3	
7.6			11	50	23	12	4	
8.2			30	66	4			
8.6			6	50	25	13	5	1
9.2		13	37	34	9	5	2	
9.25	3	29	54	12	2			
9.3	8	55	31	6				
9.4	3	37	46	12	2			
10.0		10	34	35	13	8		

In the vicinity of the studied area there are 142 observation wells in total (Fig. 2). The hydraulic groundwater head was monitored continuously from 2003. The general direction of groundwater movement is shown in Fig. 2. All extraction wells and 58 of the observation wells were used for BAM sampling. The general plume of BAM contamination is shown in Fig. 4.

Table 3. *Historical events relevant to the supply of drinking water to the municipality.*

Year	Event
1898	Water was pumped from the lake Nydalasjön
1913	Water was pumped from an extraction well established close to the lake Piparbölesjön. It was located about 1.5 km north of the Kulla extraction wells.
1954	The extraction wells and the water utility of Forslunda were established
1969	Infiltration of river water via ponds began
1975	The extraction well at Piparbölesjön was closed
1976	The extraction wells at Kulla were established and were planned as a reserve water supply. However, the water quality proved to be so good that they were continuously used as a water supply.
1981	The extraction wells at Kulla were closed and set aside as a reserve water supply
1988	The extraction wells at Kulla were opened again and were continuously used as a water supply
2007	The extraction wells at Kulla were stopped for water production and used instead as remediation wells for the BAM contamination

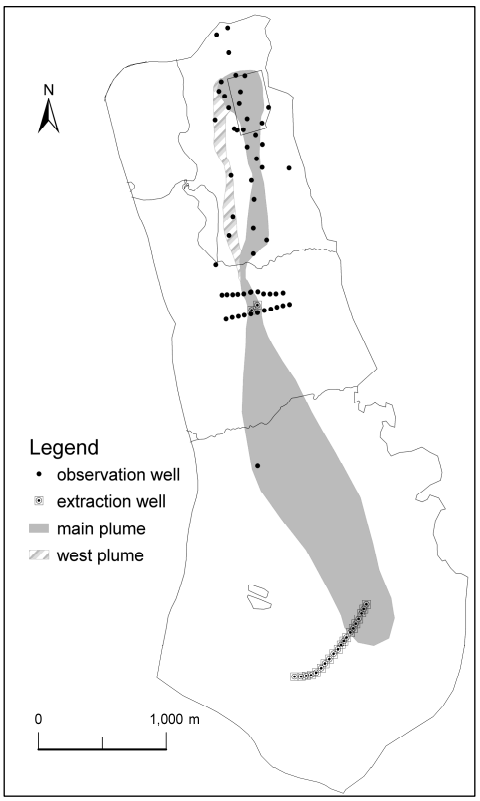

Figure 4. The general picture of the BAM contamination based on samples from observation wells and extraction wells. The west plume has less BAM concentration than the main plume.

2.3 Modeling approaches (Papers I-IV)

In the enclosed papers different modeling tools of varying complexity were used to calculate flow and transport in the vadose and groundwater zones (Table 4 and Figs. 5 and 6). The study area was progressively widened until it finally covered about 2 km × 5 km and extended from the nursery in north to the well chain in south (Fig. 2). Since the field studies proceeded over a long time-period, different amounts of data were available for each of the models. In particular, the amount of BAM data increased, although the fundamental data that were used to develop the conceptual models remained the same.

Table 4. *Overview of the modeled areas and the models used to simulate subsurface water flow and mass transport in the enclosed papers. 'Mass-balance' corresponds to a simple mass-balance model used with Monte-Carlo simulations, and HYDRUS-1D, MODFLOW, MT3DMS and FEFLOW are all distributed models.*

	Vadose zone model	Groundwater model		Modeled area
	Water flow, mass transport	Water flow	Mass transport	
Paper I	Mass-balance	Mass-balance	Mass-balance	Piparböle-Kulla
Paper II	HYDRUS-1D	-	-	Piparböle
Paper III	HYDRUS-1D	MODFLOW	MT3DMS	Piparböle-Kulla
Paper IV	HYDRUS-1D	FEFLOW	FEFLOW	Piparböle-Forslunda

2.3.1 Simple mass-balance model (Paper I)

The objective of this study was to estimate the contaminant transport through the soil and in groundwater flowing from the nursery in Piparböle to the extraction wells at Kulla (Fig. 2), using a stationary, non-distributed mass-balance model. The Monte-Carlo simulation technique was used to quantify the uncertainty of the results and to evaluate the sensitivity of the parameters that were used.

To correspond with the analysis of soil textures (Table 2), the vadose zone was divided into two appropriate texture classes. A simplified piston-flow model was applied, implying that the infiltration rate (I) and the total amount of water in the profile were constant:

$$I = \frac{\theta d}{t}, \qquad \text{(Eq. 11)}$$

where θ is the volumetric water content; d is the depth to groundwater; and t is time.

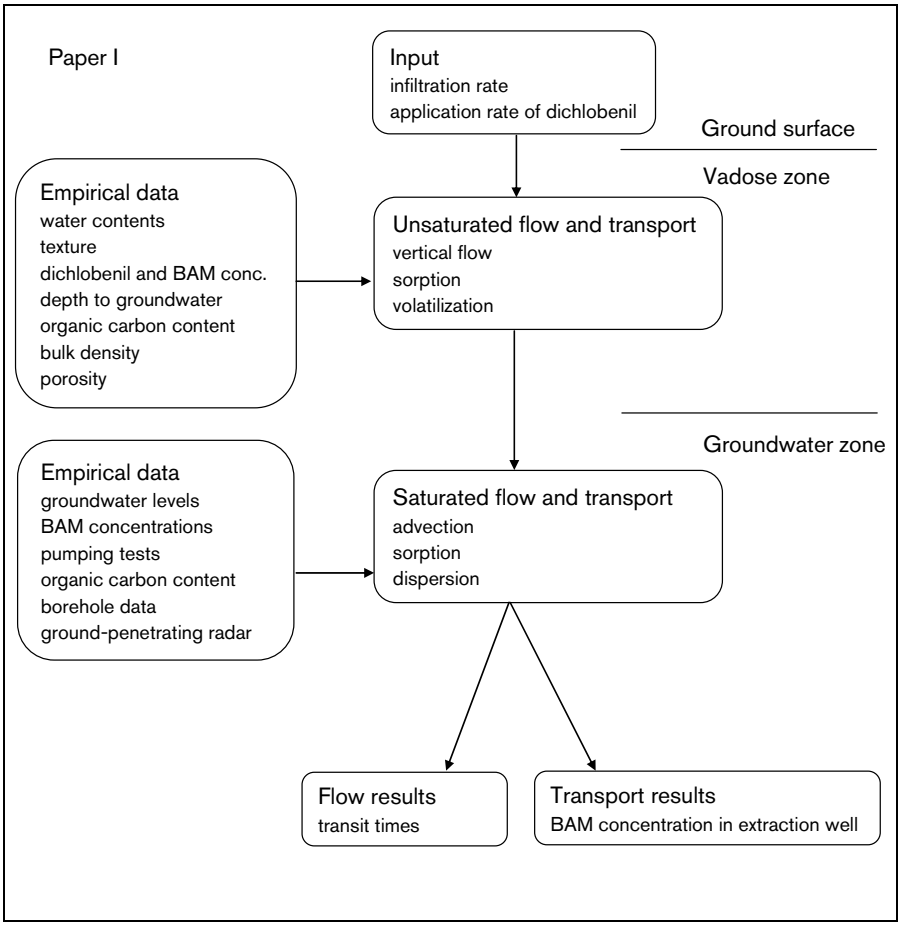

Figure 5. Empirical data and simulated processes as applied in Paper I.

Dispersion (Eq. 3) was not directly modeled, but indirectly represented by the use of Monte-Carlo simulations to calculate contaminant transport within a range of values to give various outcomes.

The linear Freundlich isotherm was applied for sorption (Eq. 5). For simplicity, degradation was neglected since under field conditions the half-lives are known to be of the order of many years (Clausen *et al.*, 2002). To estimate the BAM concentration of the soil pore water, the fugacity approach was used (Mackay, 1991), that is, the soil pore water concentration was calculated from the total concentration in the soil, assuming it to be inversely related to advection, sorption and volatilization.

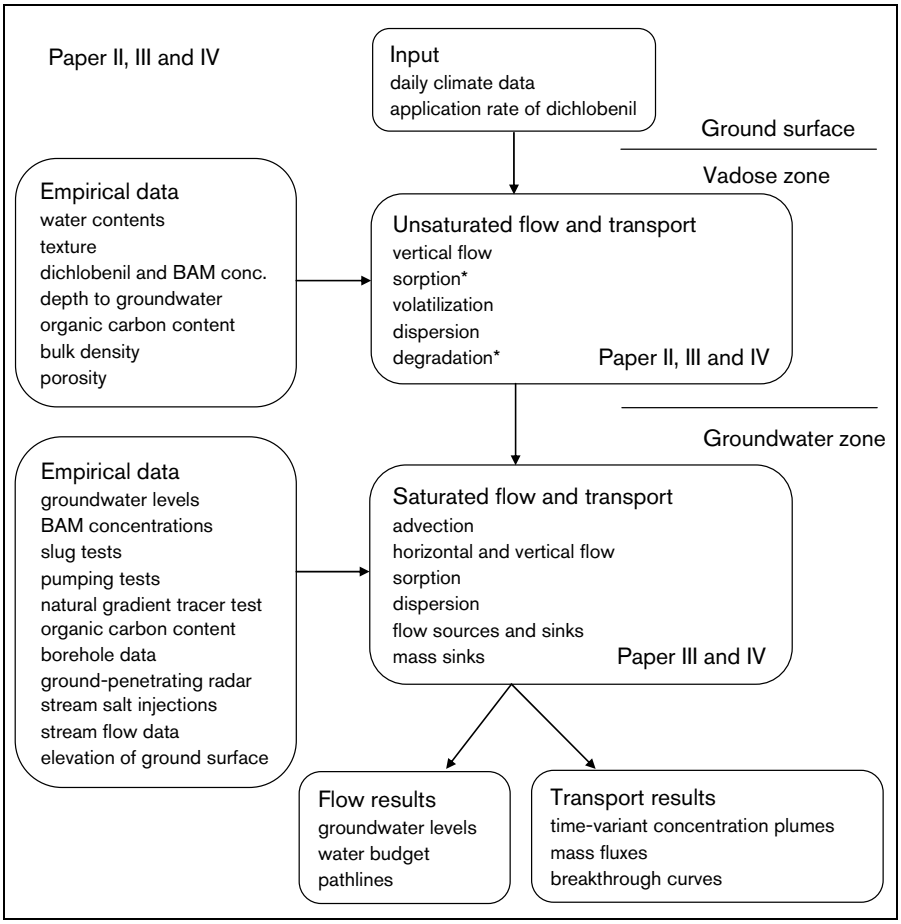

Figure 6. Empirical data and simulated processes as applied in Papers II, III and IV. Note that Paper II only was used to model the vadose zone, whereas the other papers also included the groundwater zone. The geographical scale in Papers III and IV were different. Whereas Paper III included the area down to Kulla, Paper IV encompassed the entire area to the extraction wells shown in Fig. 2. The *) indicates that the modeling procedure in Paper II were modified before it was applied in Papers III and IV.

The hydraulic conductivity in groundwater (Eq. 9) was calculated by balancing areal recharge and outflow using Darcy's law at five cross-sections along the flow direction between the nursery and the extraction wells at Kulla:

$$IA_i = h_i w_i K_i \left(\frac{dh}{dL} \right)_i , \qquad \text{(Eq. 12)}$$

where I is the infiltration rate; and at cross-section i, A is the catchment area; h is the thickness of the aquifer; w is the width of the aquifer; K is the

hydraulic conductivity; and dh/dL is the hydraulic gradient along the flow direction L. The mean value of runoff data from the small, nearby catchment of the river Sävar was used to estimate the infiltration rate, I. For each cross-section the catchment area, A, was defined by groundwater measurements and the elevation of ground surface. The thickness of the aquifer, h, at the cross-sections was derived from the evaluation of borehole data and from ground-penetrating radar measurements. The resulting K-values varied between 1.0×10^{-4} m s^{-1} and 4.7×10^{-4} m s^{-1}.

Dispersion in groundwater (Eq. 10) was assumed to be proportional to the length scale, that is, the distance between the nursery and the contaminated extraction wells at Kulla. To calculate the concentrations at the extraction wells a dilution-factor method (USEPA, 1996) was used. This method accounted for dispersion, aquifer thickness, infiltration rate, the source's width and length, the distance to the extraction well, and dilution due to regional groundwater flow, which was estimated from the results of two pumping tests.

The following is to clarify the procedure used in Paper I: i) For calculation of transit times in groundwater the length of the contaminated area, L, and the distance from the source to the extraction wells, X, were used. Unfortunately, these symbols were mixed up in the definition of the equation (Eq. 4 in Paper I). ii) In Paper I there is a map (Fig. 1 in Paper I), which shows a water divide at the east side of the Piparböle lake. From ground-penetrating radar measurements it has been found that the lake is underlain by layers of silt and clay and the water divide corresponds to the upper aquifer, i.e. there is shallow groundwater flowing into the Northern part of the lake Piparbölesjön. However, the direction of groundwater flow shown in Fig. 2 corresponds to the lower aquifer, i.e. there is groundwater flowing in the about 30 m thick esker underlying the low-permeable bottom of the lake.

2.3.2 Vadose zone modeling at soil profile scale (Paper II)

The purpose of this work was to simulate the transport of dichlobenil and BAM in the vadose zone of the nursery at soil profile scale. To this end, the physical and chemical results gathered from the 10 m deep soil sampling performed in 2003 were used.

The finite-element model HYDRUS-1D (Šimůnek *et al.*, 1998) was used to simulate vertical, unsaturated water flow and transport of dichlobenil and BAM. HYDRUS-1D is a one-dimensional model which accounts for a variety of processes, including soil-water flow, immobile water, macropore flow, solute transport, heat transport, sorption, degradation, volatilization, crop

uptake and surface runoff. The program numerically solves the Richards equations for variably saturated water-flow (Eq. 1) and advection-dispersion type equations for solute transport (Eq. 7). In a review by Köhne *et al.* (2009) it was concluded that HYDRUS-1D was one of three leading model systems for simulating pesticide transport in structured field soils.

Based on the soil sampling, the model profile was discretized into uniformly spaced elements in which the flow and transport equations were solved algebraically. To correspond with the analysis of soil textures (Table 2), the vadose zone was divided into ten appropriate texture classes. Based on the soil sampling, the van Genuchten-Mualem model (Eq. 2) was applied to describe the soil hydraulic properties, which were assumed to be unaffected by temperature. Daily climate data from 1979 to 2003 were used to run the model, which was calibrated against measured water contents. Dispersion was assumed to be proportional to the water content (Eq. 3) and the dispersivity was set to 10 % of the depth of the soil profile.

The soil sampling point was identified as a hotspot where, 1.7 g m^{-2} of the active substance dichlobenil had been applied twice a year during the period 1980 to 1991. This corresponds to the maximum recommended application rate. It was assumed that the non-linear Freundlich sorption isotherm (Eq. 5) was applicable. The sorption and degradation coefficients of dichlobenil were initially set in accordance with the results of a Danish field study (Clausen *et al.*, 2002), but were later calibrated to correlate with the measured concentrations of dichlobenil in the solid and dissolved phases. The final predictive simulation was run up to the year 2019 (Fig. 7a).

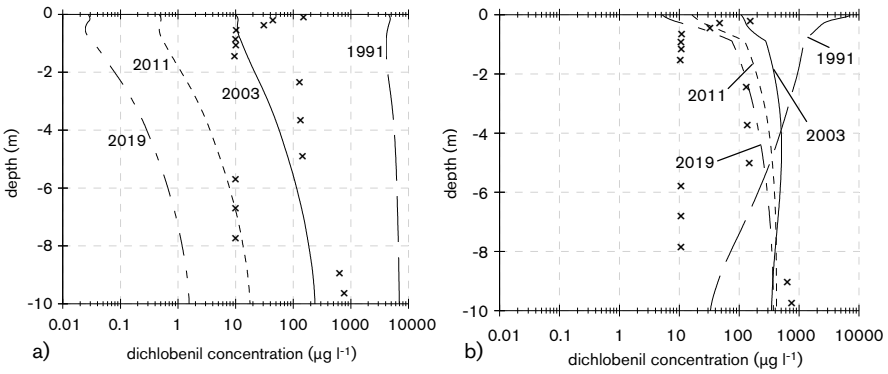

Figure 7. Soil profiles with simulated concentrations of dichlobenil from the years 1991, 2003, 2011 and 2019 using the model parameters as described in Paper II (a), and after adjustments of sorption and degradation rates as described below in Paper III (b). Analyzed concentrations from 2003 are marked with an 'x', and those that fell below the detection limit are plotted at 10 µg l^{-1}.

2.3.3 Hydrogeological modeling at regional scale (Paper III)

The objectives of this study were: (1) to model and identify significant processes that govern subsurface transport in extensive glaciofluvial and littoral sediments, while focusing on the contamination by BAM between Piparböle and Kulla; and (2) to design and test a remediation strategy and validate the results from the model. To evaluate the robustness of the model's predictions, a sensitivity analysis was undertaken with respect to the physical and chemical parameters included in the model.

Time-variant, subsurface flow and mass transport from the nursery's soil surface to the extraction wells at Kulla were simulated with the coupled models HYDRUS-1D, MODFLOW (Harbaugh *et al.*, 2000) and MT3DMS (Zheng & Wang, 1999). MODFLOW is currently the most commonly used distributed numerical model applied to three-dimensional groundwater flow problems. MT3DMS is designed to interface with the MODFLOW code and calculates the contaminant transport (Eq. 10). To calculate groundwater flow, MODFLOW uses the finite difference method (FDM), where the derivative expressions of Eq. 9 are replaced by approximate, equivalent difference quotients. The model area is discretized by mutually perpendicular lines that may be variably spaced (Fig. 8a). In three dimensions the grid system consists of boxes, which may be of varying thickness. One grid cell can have one neighbor per side, and the finite differences are computed algebraically between neighboring cells, with the calculation base in the center of the cells. For each time-step MODFLOW computes the flow rates and the cumulative volume balances from each type of inflow and outflow.

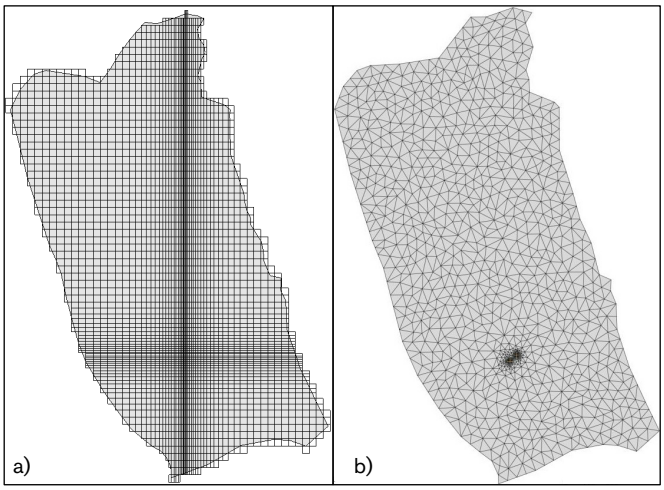

Figure 8. Examples of calculation grids using the finite-difference method (a), and the finite-element method (b).

Since the point-scale model presented in Paper II was calibrated with data sampled at a hotspot, the vadose zone model was rerun in order to generate a correct mass-balance for the total nursery area. It was assumed that the minimum recommended application rate of 0.17 g m^{-2} had been applied twice a year between 1976 and 1983, and once a year between 1984 and 1991. However, as the weed-killer has been applied to approximately 4 % of the total nursery area, and the soil has been repeatedly mixed over the years, the same amount of pesticide was assumed to have been spread over the total nursery area. In comparison with the model run in Paper II, this corresponds to a mean load of 0.0068 g m^{-2}, i.e. 4 % of 0.17 g m^{-2}. The computed BAM concentration that served as input to the groundwater model is shown in Fig. 9.

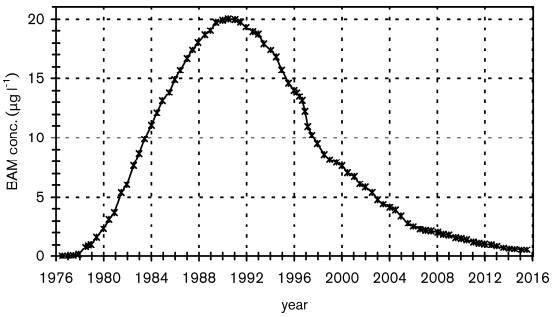

Figure 9. Concentrations of BAM at the groundwater table of the nursery, as calculated with HYDRUS-1D (Paper III).

In between the half-year-long time-steps, the discretized input of BAM concentration was assumed to follow a linear function. Overall, this means that 19 kg of the active substance, dichlobenil, had been applied to the total nursery area between 1976 and 1991. During the rerun process, the following minor adjustments of sorption and degradation rates were performed. It was assumed that the Langmuir sorption isotherm (Eq. 5) was applicable. The half-lives of degradation between depths of 0.34 and 0.90 m were adjusted from 220 to 350 days in order to achieve a better match between the observed and simulated concentrations in groundwater. For comparison with the model presented in Paper II, the effect that the changed parameters had on the simulated dichlobenil concentrations are shown in Fig. 7b.

The model was also used to study the effect of mobile and immobile water. However, since the inclusion of these different waters did not improve the model performance, and would lead to over-parameterization, the two-domain approach was abandoned.

For groundwater simulations, the model area (Fig. 2) was discretized into 20 m quadratic grid cells, uniformly sized in plane view, but with varying

thickness. The hydraulic conductivity was assumed to be isotropic and was assigned in zones whose extents were derived from the evaluation of 91 borings, from ground-penetrating radar measurements, and by using prior geological knowledge of how the glaciofluvial sediments were deposited. Two material zones were identified in the vertical direction and the model was divided into two corresponding grid layers. Although the coarse grid resolution in the vertical direction triggers numerical dispersion, the poor spatially resolved observations of BAM did not justify any finer resolution being attempted. The bedrock surface defined the bottom elevation of the model, except in small areas where more silt or clay is deposited beneath more coarse-grained materials. All hydraulic conductivity zones were manually calibrated to obtain an adequate match between the observed and calculated hydraulic heads, as well as to maintain the water balance of the aquifer.

Since the aquifer is unconfined at the extraction wells where the groundwater storage is mainly affected by pumping, the specific storativity (Eq. 9) was described by the specific yield. The specific yield was estimated from two pumping tests conducted in the study area (Fig. 2). The dispersion (Eq. 10) was calibrated with the least-squares method to optimize the correlation of the simulated with the observed concentrations of BAM in the groundwater at the nursery and at the extraction wells.

A transient validation of the model was conducted using data from a 10-day pumping test performed in the extraction wells at Kulla. The validation was also used to confirm that the mean of the specific yield, evaluated from the pumping test, was accurate. The calibrated model was then used to optimize the location, dimension and the number of new extraction wells needed for remediation purposes. Two new extraction wells were established at the nursery and a 7-day pumping test was conducted in order to validate the calibrated hydraulic conductivity values and the predicted BAM concentrations. The simulation started on 1st January 1976 and the predictive simulation was run for 45 years until 31st December 2020.

2.3.4 Hydrogeological modeling at regional scale (Paper IV)

The objective of this study was to combine the use of stable isotope data and distributed numerical modeling in order to identify the sources of extracted well water at Forslunda, and to optimize the management of the BAM-contaminated drinking water aquifer. The hypothesis was that it should be possible to redirect the contaminant plume by adjusting the input flow from the infiltration ponds.

To simulate transient, subsurface flow and mass transport from the nursery's soil surface to the extraction wells at Forslunda, the vadose zone model HYDRUS-1D was coupled to FEFLOW (Diersch, 2009). FEFLOW, with its old version of the graphical user interface, has been reviewed by Trefry and Muffels (2007). The program uses finite-element analysis to solve the groundwater flow equation of both saturated (Eq. 9) and unsaturated conditions (Eq. 1), as well as mass (Eqs. 7 and 10) and heat transport, including fluid density effects and chemical kinetics for multi-component reaction systems. For calculations with the finite-element method, the PDEs are approximated by numerically stable, piecewise, continuous functions. The model area is usually discretized horizontally into triangular elements of varying size (Fig. 8b), but rectangular elements are also possible. In 3-D, layers of varying thickness can be defined. For each time-step the computations are executed on the element nodes and the flow equation is solved algebraically for the hydraulic head.

Although FEFLOW can simulate unsaturated water-conditions, the same HYDRUS-1D model as described in Paper III was used for this process in order to save computation time. For the calculation of groundwater flow, the horizontal model area (Fig. 2) was discretized into triangular elements of varying size and thickness. In areas where mass transport was expected, the element length was no more than 20 m, i.e. less than four times the dispersivity. To avoid numerical dispersion and to get reasonable computing times in the transient model, a minimum distance of 5 m between element nodes was assigned around the wells. The hydraulic conductivity was assumed to be isotropic and was assigned to zones whose extents were derived from the evaluation of 142 borings and from ground-penetrating radar measurements. Vertically, two material zones were identified, but the upper layer was divided into two model layers in order to improve numerical accuracy in areas with large changes in hydraulic conductivity.

The model was calibrated in stationary mode in order to obtain a sufficient match between the observed and calculated hydraulic heads. Validation was performed in transient mode with time-variant hydraulic head data, the oxygen-18 isotope tracer information, and the BAM contamination data. The transient transport simulation was set to start on 1st January 1976 and was run until 31st December 2010.

2.3.5 General assumptions

Over a period of two years, daily observations of the hydraulic head from an observation well, located at the nursery, show that the difference between the maximum and minimum hydraulic head was 0.26 m with a standard

deviation of 0.06 m (Fig. 10). The variation of groundwater head was small in comparison to the depth of the vadose zone, which is 9 to 10 m, and accordingly, it was reasonable to assume a constant depth of the vadose zone.

At the nursery, no surface runoff was assumed because of the flatness and texture of the soil surface. Neither was lateral flow assumed, although preliminary evaluation of measurements of the stable isotope oxygen-18 in the soil profile, sampled at the nursery in 2003, indicated tilting soil layers (Paper II, conclusions). However, the final evaluation of the performed oxygen-18 measurements proposed that the results were biased by irrigation and the concept of tilting layers could not be justified. Comparison of soil water contents measured with the soil moisture probe in two different observation wells showed similar values at corresponding soil depths. Furthermore, the five soil profiles that were sampled in 2009 did not indicate any influence of tilting sand layers.

Almost no clay particles were found, and sorption of dichlobenil to organic matter was described by the sorption coefficient of soil organic carbon (Eq. 6). This relationship has been found to be valid for dichlobenil as long as the total organic carbon content exceeds 1 g kg^{-1} (Clausen *et al.*, 2004). Results from a field study on degradation of dichlobenil showed that sorption and desorption processes did not limit the degradation rate, probably in consequence of a fast desorption rate (Clausen *et al.*, 2007). The desorption rate of dichlobenil was therefore assumed to be fast relative to the water flow rates, and kinetic desorption was neglected.

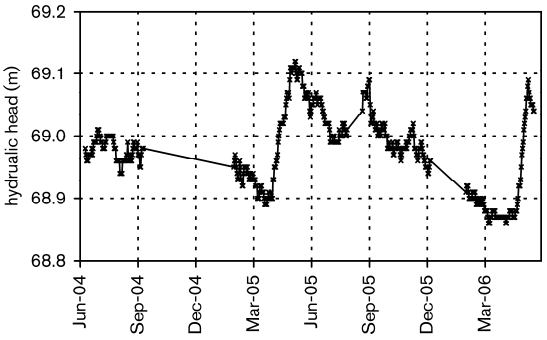

Figure 10. Observations of groundwater level at the nursery.

It has been found that different redox conditions do not affect the degradation of dichlobenil (Clausen *et al.*, 2007). The same authors have proposed that the degradation of dichlobenil to BAM is a microbiologically mediated process (Fig. 3), which can be described by first-order kinetics (Eq. 8). Since the variability of temperature is reduced with soil depth temperature independence of degradation was assumed (Holden & Fierer,

2005). Any effect that temperature can have on the degradation, mainly close to the soil surface, was thus assumed to be smoothed out through dispersion in the 10 m deep vadose zone. Further degradation of BAM has not been found under field conditions (Clausen *et al.*, 2007).

In many studies, it has been demonstrated that preferential flow can occur in sand, but many of these investigations have been conducted under unrealistic field conditions. Flux is, indeed, applied in non-ponding conditions (Malone *et al.*, 2004; Nilsson *et al.*, 2001; Geiger & Durnford, 2000), but in general the irrigation rate is close to the saturated hydraulic conductivity causing pressure heads that do not normally occur. Typically, sand has a saturated hydraulic conductivity between 1×10^{-5} m s^{-1} and 1×10^{-3} m s^{-1}, which corresponds to irrigation rates between 40 mm h^{-1} and 4000 mm h^{-1}. For example, in Umeå, rain with an intensity of 20 mm per half an hour occurs once in ten years. Since sandy soils naturally contain a high number of large pores, they permit infiltration when exposed to heavy rainfall. Kjær *et al.* (2005) studied vadose zone processes and pesticide transport at various field sites and, over a two-year period, found no leakage from the most coarse grained site. They concluded that one of the reasons must be a lack of macropores in the coarse, unstructured, sandy soil. Similar results were found by Brown *et al.* (2000), who studied the leaching of pesticides under field conditions in five contrasting soils. In accordance with the findings reported in the literature, macropore flow was not included in the models applied to the Piparböle site.

The aquifer thickness at the nursery varies between 6 and 10 m, but the variation of the groundwater level is rather small (Fig. 10). A constant recharge to groundwater was therefore assumed.

For sorption in groundwater, the linear Freundlich isotherm (Eq. 5) was applied, based on the organic carbon content (Eq. 6). Since only BAM was detected in our aquifer, and since only an insignificant degradation of dichlobenil and BAM has been observed in groundwater (Clausen *et al.*, 2007), only the transport of BAM was calculated (Eq. 10).

The specific yield represents the pore space that is emptied when the groundwater table is lowered, e.g. by pumping. The kinematic porosity (Eq. 10), defined as the effective porosity in Paper I, was assumed to equal the specific yield, which in turn was calculated from two pumping tests conducted in the study area (Fig. 2). This assumption implies that the kinematic porosity was slightly underestimated, since also a part of the non-drained volume fraction contributes to the flow.

2.3.6 Specific properties of the applied distributed models

The models used for groundwater modeling using the finite-difference (FDM) and the finite-element methods (FEM) were MODFLOW and FEFLOW, respectively. There are some important differences between these models. While the finite-difference grid is restricted to rectangular shapes, the finite-element mesh is appropriate for more complex geometries. A FEM mesh allows local refinement around central parts of the model without the need to introduce an unnecessary level of resolution of peripheral areas (Fig. 8). In both approaches it is important that the cell size does not differ much from its nearest neighbor. However, in FEM, the mesh should be constructed with care in order to avoid the angles of the mesh triangles being too small or too large. Since the calculations in FEM are performed on the nodes, and not in the centre of the cells, layer properties in the vertical direction are amalgamated and hydraulic conductivity becomes a mixture of, for example, its values for sand and clay. This has a large influence on particle tracking and solute transport. Therefore, to obtain accurate velocities in models with a low-permeable layer, either above or below a high-permeable layer, it is necessary to subdivide the layer with low hydraulic conductivity into two model layers.

In MODFLOW, the model grid is fixed. If a grid cell goes 'dry' because the groundwater table drops, the cell becomes inactive. Although a rewetting option is available, MODFLOW often encounters stability and convergence problems when the conditions are such that the groundwater table fluctuates across layer boundaries. In FEFLOW, the grid cells are allowed to go dry if phreatic settings are used, but it is also possible to adapt moveable mesh conditions in the vertical direction. Since FEFLOW can model unsaturated conditions, it can manage perched water conditions through the Richards equation (Eq. 1) or by scaling hydraulic conductivity according to the thickness of the saturated layer. In MODFLOW, time discretization must be specified beforehand, while in FEFLOW it is adaptively refined according to the time resolution of flows and the magnitude of derivative changes of hydraulic heads. Generally, the mathematical descriptions in FEFLOW are more closely connected to the physical processes that are being simulated, than they are in MODFLOW.

3 Results

3.1 Modeling results

The concentrations of BAM in the Kulla extraction wells were calculated with the simple mass-balance model (Paper I) as well as with the transient, distributed model (Paper III). Specific model results and observed BAM concentrations are reported in the respective article (Papers I-IV). The calculated range of BAM concentrations, as given by the Monte-Carlo simulations, is shown in Fig. 11. Since the stationary model was based on observed BAM concentrations at the nursery in 2003 the calculated concentrations correspond to this year. The most probable value was 0.2 μg l^{-1}, with 50 % of the BAM concentrations exceeding 0.6 μg l^{-1}. With the distributed model the BAM concentrations were calculated for both stationary and time-variant groundwater flow (Fig. 12). In comparison with the observed BAM concentrations, the mass-balance model generally over-predicted the concentration, while the transient result of the distributed model gave a correlation coefficient between 0.40 and 0.61, dependent on which of the two extraction wells the samples were assumed to be taken from (Paper III).

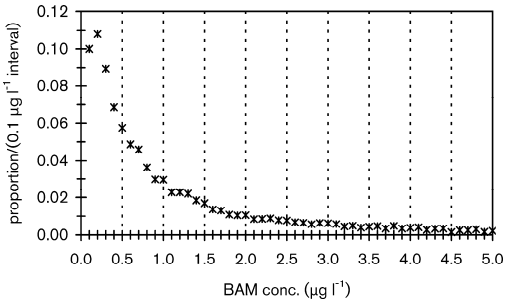

Figure 11. Predicted BAM concentrations in the Kulla extraction well calculated with Monte Carlo simulations (Paper I). The accuracy of the data points is 0.1 μg l^{-1}. All proportions sum to 1.0. In the plot, 840 of a total of 10 000 calculations are outside the visible range.

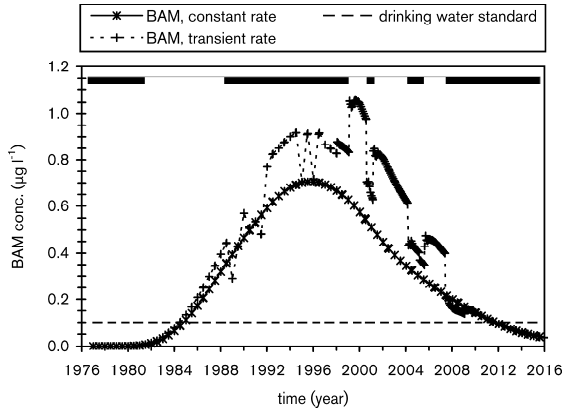

Figure 12. BAM concentration in the western extraction well at Kulla, simulated at constant and transient extraction rates (Paper III). The transient extraction rate varied between 0 and 65 l s^{-1}. The constant extraction rate was 44 l s^{-1}, which corresponded to the transient rate from February 2009. The black bar at the top of the graph indicates that the two wells were running; the white bar indicates that they were closed. The European drinking water standard is 0.1 µg l^{-1} for pesticides.

The calculated median transit times for BAM and water were all similar within the vadose zone, but differed in the groundwater zone where they were 1.6 (water) to 1.7 (BAM) times longer in the distributed models compared with the mass-balance model (Table 5). The similarity of transit times for BAM and water in the vadose zone is probably a consequence of the thickness of the zone, which results in a transit time for water of four years. In the two models this means that the different time resolution of the infiltration rates has only a small effect on transit times.

Table 5. *Median transit times for BAM and water from the soil surface at the tree nursery, through the vadose zone to: the groundwater table; the extraction wells at Kulla; and the extraction wells at Forslunda. The calculated values come from the simple mass-balance model (Paper I) and from the distributed models (Papers II, III and IV).*

From soil surface at nursery to…	BAM – transit time (y)		Water – transit time (y)	
	Mass-balance model	Distributed model	Mass-balance model	Distributed model
Groundwater	6.9	7.2	3.9	4.3
Kulla	9.9	12.3	5.7	7.2
Forslunda	-	15.6	-	9.1

In groundwater, the difference in calculated transit times for BAM and water can be explained by differences in the resolution of hydraulic conductivity and differences in aquifer thickness. In particular, the thin layers of silt that partly cover the esker were not included in the mass-balance model.

The simulation results indicated a total transit time for BAM to the extraction wells at Forslunda, which is located 4.5 km south of the nursery (Fig. 2), of about 16 years. Although the distance between the nursery and

Kulla is only half of that between Kulla and Forslunda, the transit times for BAM and water were about 50 % longer. In general, the results show that the effect of sorption, which holds back the movement of BAM in the aquifer, corresponds to a retardation factor of about 1.7; (for comparison, the retardation factor of DDT it is 40 000).

Concentrations of BAM in the well chain at Forslunda were only computed with the distributed model. The results of this model approach, validated with oxygen-18 data (Paper IV), demonstrated that managing the infiltration ponds did affect the proportions of different water sources in the extraction wells at Forslunda, which in turn have affected the observed BAM concentrations. The calculated BAM concentrations in the second well, counted from east (Fig. 2), are plotted in Fig. 13 for three scenarios that were run from February 2007:

a) simulation corresponding to actual conditions with a varying infiltration rate via the ponds and a constant extraction rate of 44 l s^{-1} in the Kulla wells
b) a constant infiltration rate via the ponds of 180 l s^{-1} and extraction at Kulla of 44 l s^{-1}
c) a constant infiltration rate via the ponds of 180 l s^{-1} and no extraction at Kulla after May 2007

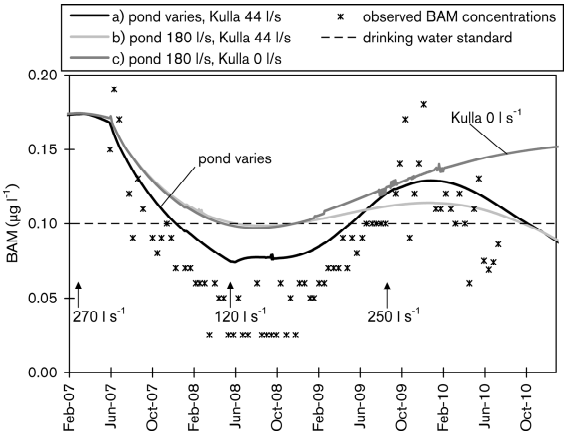

Figure 13. Observed BAM concentrations and the simulation results of three modeled scenarios at extraction well 2 (counted from east) in the well chain at Forslunda. The European drinking water standard is set to 0.1 µg l^{-1} for pesticides. The simulation with varying pumping rate to the ponds, which corresponds to the normal simulation, is indicated with arrows and text. In the scenario with no extraction at the Kulla wells the pumping rate was stopped after May 2007. The results were calculated with the model presented in Paper IV.

For all scenarios it can be seen that despite the infiltration rate via the ponds being constant, the BAM concentrations increased in 2009. If scenarios (b) and (c) are compared, the impact of the northern wells becomes evident in 2009 and 2010. Under scenario (b), the BAM concentration started to

decrease at the beginning of 2010, while under scenario (c) it continued to increase. Moreover, if the two scenarios are compared before the BAM concentration began to decrease in scenario (b), it is evident that the difference in concentrations increased. This indicates that the management of the infiltration ponds has not been the only source of impact, but that the management of the extraction wells at Kulla has also had a significant effect on the BAM concentrations observed in the well chain.

If the conditions are changed either at the ponds or at the Kulla extraction wells, a difference in delay time becomes apparent until the effect on the contaminant plume is visible at the well chain. While the median transit time between the extraction wells at Kulla and Forslunda is approximately forty months (Table 5), the oxygen-18 data and the simulation results (Paper IV) show that the transit time between the infiltration ponds and the extraction wells at Forslunda is only two to five months. During two periods over the last decade, the Kulla wells were closed (white bars at top of Fig. 12): first, from March 2001 to March 2004; then from August 2005 to May 2007. This indicates that the first closure had an effect until July 2007, and the second closure had an effect that lasted until between December 2008 and September 2010. This appears to be consistent with the varying BAM concentrations that prevailed under scenario (a), which simulated the actual conditions, as well as being consistent with the observed BAM concentrations (Fig. 4 in Paper IV). If scenarios (b) and (c) are compared, the no-extraction scenario would have its full effect, following the same reasoning, after forty months, which was in September 2010. The effect of no extraction first became evident in February 2009, which was 21 months after the wells were stopped, after which the effect intensified until the end of the simulation in December 2010.

3.2 Model uncertainties

The sensitivity analysis that was undertaken with respect to the physical and chemical parameters included in the simple mass-balance model and in the distributed model gave varying results (Table 6). The mass-balance model was sensitive both to parameter uncertainty and to the effect that a parameter has on the model outcome, whereas the sensitivity of the distributed model only were affected by the latter.

While the saturated hydraulic conductivity and the infiltration rate were the most sensitive parameters in the distributed model, the dilution factor due to regional groundwater flow, and the weight fraction of soil organic carbon were found to be the most sensitive parameters in the mass-balance

model. To some extent, the dilution factor represents those physical properties derived from hydraulic conductivity and infiltration rate in the distributed model; but the two model approaches still differ.

Table 6. *Results of the sensitivity analysis for the concentration of BAM in the Kulla extraction wells calculated with the simple mass-balance model and the distributed model. The sensitivities are expressed as percentages of the contribution to the total model uncertainty.*

Sensitivity	Mass-balance model	Distributed model
Highest	Dilution factor due to regional groundwater flow (53 %)	Hydraulic conductivity in groundwater zone (27 %)
Second highest	Weight fraction of soil organic carbon (31 %)	Infiltration rate (20 %)
Third highest	Sorption coefficient of soil organic carbon for BAM (8 %)	Tortuosity factor (8 %)

In the distributed model, there are several chemical parameters that account for the sorption and degradation of dichlobenil and BAM in the vadose and groundwater zones. This influences the sensitivity analysis since these related parameters effectively prevent each other from being allocated a high sensitivity score, whereas a single parameter, such as the weight fraction of soil organic carbon in the mass-balance model, is not prevented from receiving a high sensitivity score. Nevertheless, the influence from sorption in the mass-balance model was higher than the total influence from sorption and degradation in the distributed model. In the distributed model it was instead physical parameters, many of them van Genuchten-Mualem parameters (Eq. 2), that accounted for the high sensitivity scores.

To summarize, the three most sensitive parameters accounted for 92 % of the model uncertainty in the mass-balance model, while they accounted for 55 % in the distributed model. Except for the tortuosity factor there were additional five parameters in the distributed model that accounted for an almost equivalent degree (6 to 8 %) of model uncertainty (Table 4 in Paper III).

The effect of various extraction rates on the observed BAM concentrations can be interpreted from Fig. 12. The extraction rate varied between 0 and 65 l s^{-1} and, when the pump was stopped, the simulated BAM concentration increased due to a decreased dilution of non-contaminated water. As is apparent from the BAM concentrations, the extraction rate from the transient simulation was usually smaller than the corresponding rate from the stationary simulation, which was 44 l s^{-1}. The effect on the simulated BAM concentrations is significant and is comparable with the mass-balance model, where the dilution factor due to regional groundwater flow was

found to be the most important parameter for predicting the BAM concentration in the extraction wells.

The uncertainty of the transit-time calculations, given by the Monte-Carlo simulations, from the soil surface at the nursery to the Kulla extraction wells is displayed in Fig. 14. The highest probable transit time was 8 years, but in 50 % of the calculations the transit time exceeded 10 years. The skewness of these results derives from a number of parameters, such as the saturated hydraulic conductivity and the weight fraction of soil organic carbon, that were assumed to conform to a log-normal distribution. If a 95 % confidence interval is constructed from the results, the limits would be 5.3 to 22.6 years.

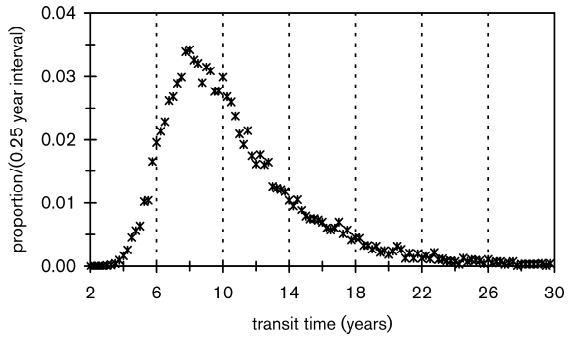

Figure 14. Predicted transit times of BAM in the Kulla extraction well calculated with Monte Carlo simulations (Paper I). The accuracy of the data points is 0.25 years. All proportions sum to 1.0. In the plot, 59 of a total of 10 000 calculations are outside the visible range.

From the calculated range of BAM concentrations in the Kulla wells (Fig. 11), the upper and the lower limits of the 95 % confidence intervals differed by a factor of 320. Compared with the difference for transit times, which was only fourfold, this clearly shows how the calculated concentrations were significantly more uncertain. The level of uncertainty surrounding the distributed models' results was decreased through validation with data from pumping tests, hydraulic head measurements, analyzed BAM concentrations, and the analyses of the stable isotope oxygen-18. The uncertainty was quantified as the 95 % confidence limit of ± 0.080 μg l^{-1}, which was derived from the standard deviation of the residuals of the observed and simulated concentrations at the Kulla extraction wells. This is significantly lower than the calculated uncertainty of concentrations in the mass-balance model.

4 Discussion

4.1 Modeling results

The results were received from a glaciofluvial esker aquifer contaminated by the aqueous phase liquid BAM. Dependent on model approach, the calculated median transit times for BAM from the source at the soil surface to the extraction wells at Kulla, located about 1.5 km down-gradient from the source, were 10 to 12 years. With the distributed model approach, the corresponding transit time to the extraction wells at Forslunda, located about 4.5 km down-gradient from the source, were about 16 years. In a simulation with the distributed model it was predicted that, due to natural attenuation, the BAM concentration in the Kulla wells will fall below the drinking water standard in 2019.

In glaciofluvial material the hydraulic conductivity is high, which might constrain the effect of dispersion in comparison with the effect of advection. The results of this study showed a limited lateral dispersal of the contaminant BAM, as it moves from the source in littoral sand to the glaciofluvial esker, which has a comparatively coarser texture and higher hydraulic conductivity. The front of the contaminant plume was actually narrowed as it reached the esker (Fig. 11 in Paper III), and the plume was found to follow the border of the esker and move directly to the extraction wells at Kulla. The limited lateral dispersal in the esker probably explains why the highly water soluble degradation product BAM can migrate in high concentrations over considerable distances. The substance was able to contaminate the groundwater extraction wells at Forslunda at levels that exceed the European drinking water standard for pesticides. The situation would have been worse if not the aquifer was reinforced by artificial recharge, and the contaminant plume was diluted by regional groundwater

flow. Furthermore, according to former employees at the nursery, the herbicide Totex was expensive and therefore modestly used. Despite this it was, however, enough to contaminate an aquifer holding large groundwater quantities.

In the literature there are many reported findings of BAM in groundwater, but to my knowledge there are few previous studies published in the peer-reviewed literature on its movement including both the vadose and groundwater zones, particularly in glaciofluvial settings.

For esker material, a modeling study has been conducted to the Honkala aquifer in Finland (Artimo, 2002). In analogy with Papers III and IV, Artimo applied a distributed model at regional scale and the contaminant plume had similar extent in length. Compared to the models in Papers III and IV, Artimo used longitudinal dispersivities that were 8 to 10 times larger, and transverse dispersivities that were 40 to 50 times larger. However, the Honkala aquifer was contaminated by the dense non-aqueous phase liquid tetrachloroethylene, and the vadose zone was not included in the modeling, which makes further comparisons difficult.

Similar to the approach adopted in Paper III, van der Grift and Griffioen (2008) performed a coupling of HYDRUS-1D to MODFLOW and MT3DMS. They applied their model to sandy sediments at regional scale, but focused on atmospheric deposition of heavy metals. In comparison to point sources located at the ground surface, pollution from atmospheric deposition commonly generates more diffuse and less bordered contaminant plumes. Although the results by van der Grift and Griffioen (2008) are not fully comparable to the ones received here they performed both historic and predictive modeling, and a sensitivity analysis showed that their model results were most sensitive to sorption parameters. In the model in Paper III it was the hydraulic conductivity in the groundwater zone that received the highest sensitivity score, while the total influence from the sorption parameters accounted for the third highest sensitivity score (Table 4 in Paper III).

Verma *et al.* (2009) presented a fuzzy set theory, similar to the Monte-Carlo simulations performed in Paper I, to model transport of the pesticide endosulfan. They included the degradation rate, but focused only on the vadose zone and applied the model on a soil profile with layers of clay, silty loam and loam.

The breakthrough curve of BAM became wide. Similar results have been obtained in previous studies on pesticide leaching in unstructured soils (Kjaer *et al.*, 2005; Brown *et al.*, 2000). This helps to explain why the BAM

contaminant was predicted to feed into groundwater at levels that may exceed the drinking water standard at the Kulla extraction wells until 2019.

However, the observed and simulated concentrations were not perfectly matched. Reasons can be both that all significant transport processes were not fully understood and included in the model, and that the quality of the analyzed BAM samples in groundwater varies. In particular, the sampling quality may vary in those samples that were collected earlier than 2007 (Paper III). In the vadose zone the dispersion process may be better determined. For example, it is not evident whether fingered flow can be a significant process at infiltration rates that normally occur at this site (Selker *et al.*, 1992). However, in this study there was no empirical data motivating the concept of fingered flow. In the groundwater models, the heterogeneous properties of glaciofluvial material were not included. The variability of hydraulic conductivity may more or less influence the pathways of contaminant transport. If the variability is high, the assumption of homogeneous zones within the aquifer might have overestimated the predicted remediation efficiency (Maji & Sudicky, 2008; Rauber *et al.*, 1998). To evaluate the importance of dispersion in the vadose zone and variability of hydraulic conductivity in the esker further investigations are needed.

4.2 Remediation strategies

The effect of the following three remediation strategies on the contaminant plume was evaluated in the enclosed papers:

(1) the removal of contaminated water through extraction wells installed close to or within the nursery field
(2) the use of the existing extraction wells at Kulla to remove contaminated water
(3) to increase the infiltration rate via the ponds in order to redirect and dilute the contaminant plume

4.2.1 The contaminant source

The first strategy, (1), illustrated in Paper III, involved optimizing the location of remediation wells. The hypothesis was that having the remediation wells located as close as possible to the contaminant source would speed up the remediation process. Two wells were established at locations where the model predicted the efficient removal of the BAM-contamination (Fig. 2). The results of a 7-day pumping test conducted in the respective wells, showed the conditions for water extraction to be good:

i) at the depth where the 2 m screened wells were established, the results indicated that it would be possible to extract more water than supplied by the catchment area; and ii) the BAM concentrations in analyzed samples corresponded with those predicted by the model. In a worst-case scenario it was assumed that the model underestimates the true BAM concentration with 0.095 μg l^{-1} at the extraction wells in Kulla. With the remediation wells, the worst-case scenario predicted that the extraction wells at Kulla would be clean in four years. The same scenario, but without the remediation wells, predicted the extraction wells to be clean in nine years (2019).

There are, however, alternative remediation strategies that can be implemented close to the source in order to hinder, modify or remove the contaminant. From the results of the mass-balance model (Paper I), it follows that the application of a carbon source, such as milled peat, spread and plowed over the open land area of the contaminated nursery field would increase the soil sorption capacity, and thus have a significant influence on the transport of BAM to groundwater. Compared with sand, peat has a much greater water-holding capacity that would further speed up the establishment of vegetation, which would in turn increase evaporation and decrease the infiltration rate. Other possible methods might include covering the area with, e.g. a sheet of ethylene-propylene rubber in order to stop infiltration; installing a continuous, permeable, reactive barrier across the contaminant plume where it moves from the nursery field in order to boost degradation, through zero-valent iron, or sorption with activated carbon; or to excavate the vadose zone. However, government authorities would probably be reluctant to implement these remediation techniques, since the area is located within the proposed primary water protection zone, and it might be problematic to control their long-term function. There are also little empirical evidence related to the *in situ* treatment effects of active barriers under field conditions (Thiruverikatachari *et al.*, 2008).

4.2.2 The recipients

Even if the spreading from the contaminant source were removed, it would still be necessary to continue with actions (2) and (3) above as temporary measures, because of the contamination of the groundwater between the nursery and the extraction wells. BAM-contaminated water from the two extraction wells at Kulla has been pumped and released down-gradient to the stream Kullabäcken, about 1 km east of the well chain, since May 2007 (Fig. 2). Because the Kulla wells are situated 1.5 km down-gradient from the contaminant source, this has not been an effective way to remediate the area. An alternative would be to install a carbon filter at the water supply, but

given the large volume of production, the initial investment and subsequent running costs would be substantial.

Both actions (2) and (3) had a significant effect on the BAM concentrations found in the well chain. However, the two actions work counter to the water balance. The Kulla wells can work as remediation wells, but as this water is contaminated it cannot be used in the production of drinking water. To balance the extracted groundwater, the artificial recharge via the ponds must increase by an equivalent amount, which would have the effect of redirecting the contaminant plume. However, increasing the load of river water into the ponds would mean increased clogging of the infiltrating surface due to physical, biological and chemical processes. This clogging would reduce the infiltration capacity of the ponds, which would then require cleaning up more frequently. It might therefore be advisable to decrease the extraction rate of the Kulla wells, although not close them, so that the load on the infiltration ponds could be reduced.

At Kulla it is important to consider the dilution factor due to regional groundwater flow, as the same amount of contaminant could be removed although the extraction rate would be decreased. Because of the water balance effect, a decreased extraction rate also means that the energy consumption for pumping would be reduced at both the Kulla wells and the infiltration ponds. Under the current management situation, where the extraction rate at the Kulla wells is about 44 l s^{-1}, the modeled scenarios suggest that a constant infiltration rate to the ponds of 220 l s^{-1} would be sufficient to avoid the drinking water standard of 0.1 μg l^{-1} being exceeded (Paper IV).

In any future scenario of contamination of the aquifer, it will be important to observe the difference in time delay between the demonstrated remediation strategies and any of the resulting effects. The infiltration ponds are suitable for implementing short-term remedial actions in response to, for example, accidents resulting in sudden loads of contaminants, which might follow from a truck accident on the road to the west of the infiltration ponds, or from an accident at the existing asphalt industry located to the north of the ponds. In these cases an increased infiltration rate would both dilute and redirect the groundwater contamination. The northern extraction wells are, nevertheless, suitable for long-term scenarios in which contaminants remain in the aquifer for many years, as is the current situation.

4.3 Modeling approaches

Different model approaches were adapted to simulate the significant processes involved in the subsurface flow and transport of an aqueous-phase-liquid in glaciofluvial and littoral sediments. The model approaches examined in the present study are expected to be relevant to other, similar settings that are or have been contaminated. However, if the vadose zone should consist of structured soils it will probably be necessary to include macropore flow. Macropore flow is, though, a process possible to simulate with the distributed model tools used.

A pre-requisite for reliable model output is good quality of empirical input data and a valid underlying conceptual model. However, if there is a lack of field data or capital to set up a distributed numerical model, the simple mass-balance model approach (Paper I) would be the preferred option. It offers the possibility of using a range of values rather than a single value, which is usually chosen to represent the worst-case, and provides more reliable first estimates of transit time and contaminant concentrations. The mass-balance model also provides an indication of the uncertainty of the result with the most sensitive parameters being made apparent. Although the conditions for dispersal may be ambiguous, the model results indicate which field data should be collected in order to reduce model uncertainty and to improve the precision of new model calculations.

However, for the best predictions, especially of degrading contaminants, a transient model is necessary. Dynamic runs were not possible with the mass-balance model adopted, and for transient processes it is preferable to use a distributed numerical model. A distributed model can improve the precision of the calculations and is superior when, for example, the hydraulic conductivity varies significantly laterally and with depth within a study area. Without necessarily having to calibrate such models, they can also provide a framework with which the conditions and dynamic processes important to improving the interpretation of a study area can be examined. Distributed models enhance the evaluation of a site, especially since they can be used to make predictions concerning the consequences of proposed actions, to simulate remediation scenarios, and to study the effects of changing management or climate change. Moreover, predicted contour maps showing contaminant concentrations over time will constitute important information in communications with authorities, managers and the public. Such contour maps are easy to produce with a grid-based model. However, the confidence of the model predictions depends on the results of the calibration, sensitivity analysis, and model validation with independent data. For example, in Paper IV, independent data were available from the analysis

of the stable isotope oxygen-18, which is useful when different water sources are present, but data from measurements of hydraulic heads and BAM concentrations were also available. In Paper IV, the hydraulic head data did validate the model behavior as long as the total water balance varied within reasonable bounds. A feature of the distributed model was that many of the parameters used proved to be nearly identical in the influence they had on model uncertainty (Paper III).

Although transient conditions are crucial when evaluating the progress of contaminant concentrations at a specific point, a distributed model with stationary flow can produce reasonable estimates. In the example from the Kulla extraction well (Fig. 12) the plot with constant pumping rate did provide an adequate estimate, although the plot with dynamic pumping conditions did give a better prediction (Paper III).

The applicability of the two model approaches is summarized in Table 7. Both model tools were intended to be used at contaminated sites classified as being a high or very high risk. In general this implies that there are sensitive recipients, for example an extraction well used to supply drinking water, at high risk of being contaminated. In the decision of what model tool to use it will be a question of considering data quality, funding, the need to predict consequences of proposed actions, and public requirements such as generic guidelines and drinking water standards. At the investigated Piparböle site the distributed model approach proved to be the best alternative, since there was a need to predict consequences of different remediation strategies, and the proximity to the drinking water aquifer required accurate calculations.

Table 7. *The applicability of the simple mass-balance model approach run with Monte Carlo simulations, and the distributed model approach.*

Simple mass-balance model	Distributed model
Stationary processes	Time-variant processes, e.g. a degrading contaminant
High conditions for dispersal	Very high conditions for dispersal
To obtain reliable estimates of transit time, not only worst-case calculations	Can simulate transport processes more accurately
To obtain first estimates of concentrations	To obtain concentration calculations at specific points
Preferable if data quality is insufficient	Requires dense field data
Indicates the most uncertain data for further sampling and improved precision of calculations	Predictions are possible, but the accuracy depends on the extent to which the model is validated
Reflects the uncertainty of the parameters	Evaluation of remediation strategies
Less expensive than a distributed model	

5 Conclusions

The field investigations and subsurface modeling revealed two methods that could be used to remediate the aquifer so that it would meet the drinking water standard. The first method was to redirect the contaminant plume via two infiltration ponds by increasing the artificial recharge rate. The second method was to use extraction wells to pump out, and hence remove the contaminant plume. For the latter method, one possibility was to use two up-gradient extraction wells, which have been normally used as producers of drinking water. It was found essential to combine these methods in order: i) to avoid clogging of the infiltration ponds by fine sediments from surface water; and ii) to balance the water budget of the aquifer. However, since the water in the two up-gradient wells is of good quality, except for the current contamination, it would be desirable to reinstate these wells into production as soon as possible. To reduce the attenuation time for the contaminant concentration in order to meet the drinking water standard at these wells, it was found that remediation wells could be established close to the contaminant source where conditions were suitable for groundwater extraction.

The model tools presented here were applied to an aquifer consisting of extensive glaciofluvial sediments. The simple mass-balance approach was found to help in generating reliable first estimates of the transit time, especially when the data quality is insufficient. In this case, the simple mass-balance model reflects the uncertainty of the result, and the sensitivity analysis indicates what further field data need to be collected in order to improve the precision of the calculations. However, if the contaminant transport needs to be calculated more accurately, the distributed numerical model should be used. To strengthen the credibility of such a model, the output should be validated with independent data from various sources, which in the present study was stable isotope oxygen-18 data, data on the

BAM contamination and time-variant hydraulic head data. The overall findings are expected to be relevant to many other sites in similar settings.

6 Future research needs

Further development of the distributed model approach requires additional field data in order to improve the quantification of the dispersion process in deep, sandy vadose zones. One way of achieving this would be to inject deuterium enriched water into the soil surface at the nursery and to sample the soil at various depths after a determined time interval. Vacuum extraction could then be used to extract soil pore water in order to analyze its isotopic composition at various depths.

Future research should also focus on characterizing the variability of hydraulic conductivity and its effect on contaminant transport in eskers. This is a delicate problem since esker aquifers are often used to supply drinking water, and because the restrictions imposed by the necessity of protecting water sources often make the field experiments for such work problematic. However, knowledge of the heterogeneous properties is important since it might influence the required time period for a proposed remediation action.

To develop the site-specific model further, the extent of the depth and width of the low-permeable soil layer located north of the well chain at Forslunda must be determined. This soil consists partly of sulfide clay, which could be a source of other contaminants, such as nickel. The concentration of nickel has exceeded the Swedish drinking water standard (20 $\mu g\ l^{-1}$) in fifteen out of the twenty extraction wells. The explanatory hypothesis is that the bottom of the sulfide clay layer is located close to the groundwater table where the nickel, which bonds to sulfides under anaerobic conditions, is dissolved when the groundwater table sinks, i.e. where oxidizing conditions occur. If the conditions that cause the unwanted nickel concentrations are clarified, the management of the aquifer supplying drinking water could be further optimized.

References

Albergaria, J.T., da Conceicao, M., Alvim-Ferraz, M. & Delerue-Matos, C. (2006). Remediation efficiency of vapour extraction of sandy soils contaminated with cyclohexane: Influence of air flow rate, water and natural organic matter content. *Environmental Pollution* 143(1), 146-152.

Artimo, A. (2002). Application of flow and transport models to the polluted Honkala aquifer, Sakyla, Finland. *Boreal Environment Research* 7(2), 161-172.

Barbash, J.E., Thelin, G.P., Kolpin, D.W. & Gilliom, R.J. (2001). Major herbicides in ground water: results from the national water-quality assessment. *Journal of Environmental Quality* 30(3), 831-845.

Brown, C.D., Hollis, J.M., Bettinson, R.J. & Walker, A. (2000). Leaching of pesticides and a bromide tracer through lysimeters from five contrasting soils. *Pest Management Science* 56(1), 83-93.

CCME (1996). *Protocol for the Derivation of Envirnomental and Human Health Soil Quality Guidelines*. Manitoba, Canada: Canadian Councils for Ministers for the Environment.

Chang, L.C., Chu, H.J. & Hsiao, C.T. (2007). Optimal planning of a dynamic pump-treat-inject groundwater remediation system. *Journal of Hydrology* 342(3-4), 295-304.

Chang, N.B., Hossain, F. & Wanielista, M. (2010). Filter Media for Nutrient Removal in Natural Systems and Built Environments: I-Previous Trends and Perspectives. *Environmental Engineering Science* 27(9), 689-706.

Chang, T.C. & Yen, J.H. (2006). On-site mercury-contaminated soils remediation by using thermal desorption technology. *Journal of Hazardous Materials* 128(2-3), 208-217.

CKB *Database of Pesticides monitored in Sweden*. [online] (25 March 2009) Available from: http://vaxtskyddsmedel.slu.se/Introduktion/. [Accessed 25 June].

Clausen, L., Arildskou, N. & Larsen, F. (2002). *Nedbrydning og sorption af dichlobenil og BAM (In Danish, English abstract)*: Danmarks Tekniske Universitet. Arbejdsrapport fra Miljøstyrelsen Nr. 35.

Clausen, L., Arildskov, N.P., Larsen, F., Aamand, J. & Albrechtsen, H.J. (2007). Degradation of the herbicide dichlobenil and its metabolite BAM in soils and subsurface sediments. *Journal of Contaminant Hydrology* 89(3-4), 157-173.

Clausen, L., Larsen, F. & Albrechtsen, H.J. (2004). Sorption of the herbicide dichlobenil and the metabolite 2,6-dichlorobenzamide on soils and aquifer sediments. *Environmental Science & Technology* 38(17), 4510-4518.

Cox, C. (1997). Herbicide factsheet. Dichlobenil. *Journal of Pesticide Reform* 17(1), 14-20.

Crommentuijn, T., Sijm, D., de Bruijn, J., van den Hoop, M., van Leeuwen, K. & van de Plassche, E. (2000a). Maximum permissible and negligible concentrations for metals and metalloids in the Netherlands, taking into account background concentrations. *Journal of Environmental Management* 60(2), 121-143.

Crommentuijn, T., Sijm, D., de Bruijn, J., van Leeuwen, K. & van de Plassche, E. (2000b). Maximum permissible and negligible concentrations for some organic substances and pesticides. *Journal of Environmental Management* 58(4), 297-312.

Diersch, H.-J.G. (2009). *Reference Manual. DHI-WASY Software FEFLOW - Finite Element Subsurface Flow & Transport Simulation System*. Berlin, Germany: DHI-WASY GmbH.

Domenico, P.A. & Schwartz, F.W. (1998). Modeling the transport of dissolved contaminants. In: *Physical and chemical hydrogeology*. 2nd. ed. pp. 372-392. New York: John Wiley & Sons, Inc.

EU (2006). Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. *Official Journal of the European Union* L372, 19-31.

Eyles, N. & Meriano, M. (2010). Road-impacted sediment and water in a Lake Ontario watershed and lagoon, City of Pickering, Ontario, Canada: An example of urban basin analysis. *Sedimentary Geology* 224(1-4), 15-28.

Geiger, S.L. & Durnford, D.S. (2000). Infiltration in homogeneous sands and a mechanistic model of unstable flow. *Soil Science Society of America Journal* 64(2), 460-469.

Gelhar, L.W. (1997). Perspectives on field-scale application of stochastic subsurface hydrology. In: Dagan, G.*, et al.* (Eds.) *Subsurface Flow and Transport: A Stochastic Approach*. 1st. ed. pp. 157-176. Cambridge: University Press.

Hantush, M.M., Marino, M.A. & Islam, M.R. (2000). Models for leaching of pesticides in soils and groundwater. *Journal of Hydrology* 227(1-4), 66-83.

Harbaugh, A.W., Banta, E.R., Hill, M.C. & McDonald, M.G. (2000). *MODFLOW-2000, The U.S. Geological Survey Modular Ground-Water Model - User Guide to Modularization Concepts and the Ground-Water Flow Process*. Reston, Virginia. : U.S. Geological Survey. Open-File Report 00-92.

Hassan, A.E. (2004). Validation of numerical ground water models used to guide decision making. *Ground Water* 42(2), 277-290.

Herbst, M., Hardelauf, H., Harms, R., Vanderborght, J. & Vereecken, H. (2005). Pesticide fate at regional scale: Development of an integrated model approach and application. *Physics and Chemistry of the Earth* 30(8-10), 542-549.

Hiscock, K.M. & Grischek, T. (2002). Attenuation of groundwater pollution by bank filtration. *Journal of Hydrology* 266(3-4), 139-144.

Holden, P.A. & Fierer, N. (2005). Microbial processes in the vadose zone. *Vadose Zone Journal* 4(1), 1-21.

Hornsby, A.G., Wauchope, R.D. & Herner, A.E. (1996). *Pesticide Properties in the Environment*. New York, USA: Springer-Verlag.

Hughes, J.D. & Liu, J. (2008). MIKE SHE: Software for Integrated Surface Water/Ground Water Modeling. *Ground Water* 46(6), 797-802.

Hunt, R.J., Coplen, T.B., Haas, N.L., Saad, D.A. & Borchardt, M.A. (2005). Investigating surface water-well interaction using stable isotope ratios of water. *Journal of Hydrology* 302, 154-172.

Jorgensen, P.R., McKay, L.D. & Kistrup, J.P. (2004). Aquifer vulnerability to pesticide migration through till aquitards. *Ground Water* 42(6), 841-855.

Kjaer, J., Olsen, P., Ullum, M. & Grant, R. (2005). Leaching of glyphosate and amino-methylphosphonic acid from Danish agricultural field sites. *Journal of Environmental Quality* 34(2), 608-620.

Köhne, J.M., Köhne, S. & Šimůnek, J. (2009). A review of model applications for structured soils: b) Pesticide transport. *Journal of Contaminant Hydrology* 104(1-4), 36-60.

Kolpin, D.W., Barbash, J.E. & Gilliom, R.J. (1998). Occurrence of pesticides in shallow groundwater of the United States: Initial results from the National Water-Quality Assessment Program. *Environmental Science & Technology* 32(5), 558-566.

Kordel, W., Egli, H. & Klein, M. (2008). Transport of pesticides via macropores (IUPAC technical report). *Pure and Applied Chemistry* 80(1), 105-160.

Krabbenhoft, D.P., Anderson, M.P. & Bowser, C.J. (1990). Estimating groundwater exchange with lakes. 2. Cailbration of a 3-dimensional, solute transport model to a stable isotope plume. *Water Resources Research* 26(10), 2455-2462.

Leistra, M. & Boesten, J.J.T.I. (1989). Pesticide contamination of groundwater in western Europe. *Agriculture, Ecosystems & Environment* 26(3-4), 369-389.

Li, J.B., Huang, G.H., Zeng, G.M., Maqsood, I. & Huang, Y.F. (2007). An integrated fuzzy-stochastic modeling approach for risk assessment of groundwater contamination. *Journal of Environmental Management* 82(2), 173-188.

Li, S.-G., McLaughlin, D. & Liao, H.-S. (2003). A computational practical method for stochastic groundwater modeling. *Advances in Water Resources* 26, 1137-1148.

Mackay, D. (1991). *Multimedia Environmental Models - The Fugacity Approach*. Chelsea, Michigan, USA: Lewis Publishers. ISBN 0-87371-242-0.

Maji, R. & Sudicky, E.A. (2008). Influence of mass transfer characteristics for DNAPL source depletion and contaminant flux in a highly characterized glaciofluvial aquifer. *Journal of Contaminant Hydrology* 102(1-2), 105-119.

Malone, R.W., Shipitalo, M.J., Wauchope, R.D. & Sumner, H. (2004). Residual and contact herbicide transport through field lysimeters via preferential flow. *Journal of Environmental Quality* 33(6), 2141-2148.

Maqsood, I., Li, J.B., Huang, G.H. & Huang, Y.F. (2005). Simulation-based risk assessment of contaminated sites under remediation scenarios, planning periods, and land-use patterns - a Canadian case study. *Stochastic Environmental Research and Risk Assessment* 19(2), 146-157.

Maxwell, R.M., Carle, S.F. & Tompson, A.F.B. (2008). Contamination, risk, and heterogeneity: on the effectiveness of aquifer remediation. *Environmental Geology* 54(8), 1771-1786.

Morvan, X., Mouvet, C., Baran, N. & Gutierrez, A. (2006). Pesticides in the groundwater of a spring draining a sandy aquifer: Temporal variability of concentrations and fluxes. *Journal of Contaminant Hydrology* 87(3-4), 176-190.

Nilsson, B., Sidle, R.C., Klint, K.E., Boggild, C.E. & Broholm, K. (2001). Mass transport and scale-dependent hydraulic tests in a heterogeneous glacial till-sandy aquifer system. *Journal of Hydrology* 243(3-4), 162-179.

Panday, S. & Huyakorn, P.S. (2008). MODFLOW SURFACT: A state-of-the-art use of vadose zone flow and transport equations and numerical techniques for environmental evaluations. *Vadose Zone Journal* 7(2), 610-631.

Pavlis, M., Cummins, E. & McDonnell, K. (2010). Groundwater Vulnerability Assessment of Plant Protection Products: A Review. *Human and Ecological Risk Assessment* 16(3), 621-650.

Prommer, H., Barry, D.A. & Davis, G.B. (2000). Numerical modelling for design and evaluation of groundwater remediation schemes. *Ecological Modelling* 128(2-3), 181-195.

Pukkila, V., Gustafsson, J., Tuominen, J., Aallonen, A. & Kontro, M.H. (2009). The most-probable-number enumeration of dichlobenil and 2,6-dichlorobenzamide (BAM) degrading microbes in Finnish aquifers. *Biodegradation* 20(5), 679-686.

Rauber, M., Stauffer, F., Huggenberger, P. & Dracos, T. (1998). A numerical three-dimensional conditioned/unconditioned stochastic facies type model applied to a remediation well system. *Water Resources Research* 34(9), 2225-2233.

Ross, M., Parent, M. & Lefebvre, R. (2005). 3D geologic framework models for regional hydrogeology and land-use management: a case study from a Quaternary basin of southwestern Quebec, Canada. *Hydrogeology Journal* 13(5-6), 690-707.

Rugner, H., Finkel, M., Kaschl, A. & Bittens, M. (2006). Application of monitored natural attenuation in contaminated land management - A review and recommended approach for Europe. *Environmental Science & Policy* 9(6), 568-576.

Saripalli, K.P., Meyer, P.D., Bacon, D.H. & Freedman, V.L. (2001). Changes in hydrologic properties of aquifer media due to chemical reactions: A review. *Critical Reviews in Environmental Science and Technology* 31(4), 311-349.

Schäfer, W. & Therrien, R. (1995). Simulating transport and removal of xylene during remediation of a sandy aquifer. *Journal of Contaminant Hydrology* 19(3), 205-236.

Selker, J.S., Steenhuis, T.S. & Parlange, J.-Y. (1992). Wetting front instability in homogeneous sandy soils under continous infiltration. *Soil Science Society of America Journal* 56, 1346-1350.

Seol, Y., Zhang, H. & Schwartz, F.W. (2003). A review of in situ chemical oxidation and heterogeneity. *Environmental & Engineering Geoscience* 9(1), 37-49.

SEPA (1996). *Development of generic guideline values*. Stockholm, Sweden: Swedish Environmental Protection Agency. Report no. 4639.

SEPA (2002). *Method of Surveying Contaminated Sites (In Swedish)*. Värnamo, Sweden: Swedish Environmental Protection Agency. Environmental Quality Criteria. Rapport 4918.

Šimůnek, J., Šejna, M. & van Genuchten, M.T. (1998). *The HYDRUS-1D Software Package for Simulating the One-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media, v. 2.0*. Riverside, CA, USA: U. S. Salinity Laboratory, Agricultural Research Service U. S. Department of Agriculture.

Soutter, M. & Musy, A. (1998). Coupling 1D Monte-Carlo simulations and geostatistics to assess groundwater vulnerability to pesticide contamination on a regional scale. *Journal of Contaminant Hydrology* 32(1-2), 25-39.

Stenemo, F., Jorgensen, P.R. & Jarvis, N. (2005). Linking a one-dimensional pesticide fate model to a three-dimensional groundwater model to simulate pollution risks of shallow and deep groundwater underlying fractured till. *Journal of Contaminant Hydrology* 79(1-2), 89-106.

Stichler, W., Maloszewski, P., Bertleff, B. & Watzel, R. (2008). Use of environmental isotopes to define the capture zone of a drinking water supply situated near a dredge lake. *Journal of Hydrology* 362(3-4), 220-233.

Strack, O.D.L. (1999). Principles of the analytic element method. *Journal of Hydrology* 226(3-4), 128-138.

Sudicky, E.A., Illman, W.A., Goltz, I.K., Adams, J.J. & McLaren, R.G. (2010). Heterogeneity in hydraulic conductivity and its role on the macroscale transport of a solute plume: From measurements to a practical application of stochastic flow and transport theory. *Water Resources Research* 46, 16.

Szucs, P., Madarasz, T. & Civan, F. (2009). Remediating Over-Produced and Contaminated Aquifers by Artificial Recharge from Surface Waters. *Environmental Modeling & Assessment* 14(4), 511-520.

Thiruverikatachari, R., Vigneswaran, S. & Naidu, R. (2008). Permeable reactive barrier for groundwater remediation. *Journal of Industrial and Engineering Chemistry* 14(2), 145-156.

Törnquist, M., Kreuger, J. & Adielsson, S. (2007) Occurrence of Pesticides in Swedish water resources against a background of national risk-reduction programmes - results from 20 years of monitoring. In: Del Re, A.A.M., *et al*. (Eds.) *Proceedings of XIII Symposium in Pesticide Chemistry - Environmental Fate and Ecological Effects of Pesticides*, Piacenza, Italy. pp. 770-777.

Travis, C.C. & Doty, C.B. (1990). Can contaminated aquifers at superfund sites be remediated? *Environmental Science & Technology* 24(10), 1464-1466.

Trefry, M.G. & Muffels, C. (2007). FEFLOW: A finite-element ground water flow and transport modeling tool. *Ground Water* 45(5), 525-528.

Twarakavi, N.K.C., Šimůnek, J. & Seo, S. (2008). Evaluating interactions between groundwater and vadose zone using the HYDRUS-based flow package for MODFLOW. *Vadose Zone Journal* 7(2), 757-768.

USEPA (1996). *Soil Screening Guidance: Technical Background Document*. Washington DC, USA: Office of Solid Waste and Emergency Response. EPA/540/R95/128.

van der Grift, B. & Griffioen, J. (2008). Modelling assessment of regional groundwater contamination due to historic smelter emissions of heavy metals. *Journal of Contaminant Hydrology* 96(1-4), 48-68.

van Genuchten, M.T. (1980). A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal* 44(5), 892-898.

Verma, P., Singh, P., George, K.V., Singh, H.V., Devotta, S. & Singh, R.N. (2009). Uncertainty analysis of transport of water and pesticide in an unsaturated layered soil profile using fuzzy set theory. *Applied Mathematical Modelling* 33(2), 770-782.

Versteegh, J.F.M. & te Biesebeek, J.D. (2003). *The Quality of Drinking Water in the Netherlands in 2001 (In Dutch)*: Rijksinstituut voor Volksgezondheid en Milieu. RIVM-rapport nr. 703719003.

Weill, S., Mouche, E. & Patin, J. (2009). A generalized Richards equation for surface/subsurface flow modelling. *Journal of Hydrology* 366, 9-20.

Wolter, R., Rosenbaum, S. & Hannappel, S. (2001). The German groundwater monitoring network. In: *Proceedings of Monitoring Tailor-Made III*. pp. 277-282.

Wong, H.S. & Yeh, W.W.G. (2002). Uncertainty analysis in contaminated aquifer management. *Journal of Water Resources Planning and Management-Asce* 128(1), 33-45.

Younes, M. & Galal-Gorchev, H. (2000). Pesticides in drinking water - A case study. *Food and Chemical Toxicology* 38, S87-S90.

Zhang, K., Li, H. & Achari, G. (2009). Fuzzy-stochastic characterization of site uncertainty and variability in groundwater flow and contaminant transport through a heterogeneous aquifer. *Joumal of Contaminant Hydrology* 106, 73-82.

Zheng, C. & Wang, P.P. (1999). *MT3DMS. A Modular Three-Dimensional Multispecies Transport Model for Simulation of Advection, Dispersion, and Chemical Reactions of Contaminants in Groundwater Systems; Documentation and User's Guide*. Tuscaloosa, Alabama, USA: Department of Geological Sciences. Contract Report SERDP-99-1.

Zhou, Q.L., Birkholzer, J.T., Javandel, I. & Jordan, P.D. (2004). Modeling three-dimensional groundwater flow and advective contaminant transport at a heterogeneous mountainous site in support of remediation. *Vadose Zone Journal* 3(3), 884-900.

Acknowledgements

The work of this thesis was co-funded by Tyréns AB, Northern Sweden Soil Remediation Centre (MCN, via grants from the European Structural Funds and New Objective 1), the Swedish University of Agricultural Sciences (SLU) and the Swedish Defense Research Agency (FOI).

I would like to express my sincere gratitude to all colleagues, friends and family who have supported me during my time as a PhD-student and made this possible.

Under arbetets gång är det många som jag mött längs vägen. Det har varit många trevliga möten, givande samtal och muntra tillrop. Även om jag kanske inte varit så bra på att närvara på fikaraster och luncher under den senaste tiden uppskattar jag verkligen alla pratstunder. Tack alla ni!

Jag riktar ett varmt tack till Harald Grip som var min första huvudhandledare. Halvvägs in i arbetet gick du i pension men har ändå funnits med hela vägen fram mot målet. I arbetets inledningsskede var din fina förmåga att inspirera till fältförsök och av ingenting bygga upp fältutrustning mycket viktig. I skrivprocessen har du bidragit med din breda kunskap och analysförmåga inom hydrologi och hydrogeologi.

Stort tack till Hjalmar Laudon som gick in som huvudhandledare efter Harald. Hjalmar, trots att du kastades mitt in i projektet när större delen av fältarbetet var avklarat såg du nya möjligheter. Du har haft ett stort engagemang, funnits tillgänglig, och inspirerat när det känts tungt. Med din förmåga att styra upp och hitta den vetenskapliga kärnan har du bidragit mycket till avhandlingens slutliga form.

Jag tackar Ulf Wiklund som var en av initiativtagarna till doktorandprojektet och sökte finansiering från Tyréns stiftelse. Det var avgörande för att jag skulle få tjänsten som industridoktorand på Tyréns. Ulf, du har en enastående energi och initiativförmåga och ett engagemang som sträcker sig utöver det vanliga. Problem som saknar lösningar finns inte. För

mig har det varit värdefullt att ha en länk till verkligheten och du har hela tiden serverat inspirerande arbetsuppgifter från ”andra sidan”. Detta har gett perspektiv på doktorandarbetet, och i stunder då jag kört fast har det fått mig att tänka på annat. Men arbete i riktiga projekt har även gett direkt inspiration till vad som är viktigt att lyfta fram i doktorandarbetet. Jag ser fram emot att jobba mer med dig framöver!

Stort tack till Jan Sjöström som var min biträdande handledare längs hela resan. Janne, du såg till att jag kunde arbeta på FOI där det finns kompetens inom modellering och föroreningsspridning. Du har varit en fin länk mellan forskarvärlden och verkligheten och hela tiden kommit med praktiska synpunkter i arbetet. Däremellan har du kryddat tillvaron med underfundiga skämt.

På FOI har jag också fått hjälp av Jan Burman och Jeff Lewis. Tack för era värdefulla synpunkter och inspel i modelleringsarbetet!

Personal på Umeva, det kommunala vatten- och avfallsbolaget i Umeå, har hjälpt mig med information och arkivsökning. Tack!

Tack till Susanne Rutqvist och Kristina Frech som hjälpte mig med kemiska analyser i tidig fas av projektet. Susanne gjorde också sitt examensarbete utifrån data från Piparböle, vilket var till hjälp i mitt arbete.

Jag tackar mina föräldrar, Maj-Lis och Lars, och min bror, Magnus, som på olika sätt inspirerat mig till att nå hit. Tyvärr bor vi numera lite långt från varandra, men jag har i alla fall slutat att flytta 60 mil vart 5:e år.

Hanna, min livskamrat och stora kärlek, din familj och vänner har ställt upp mycket senaste tiden för att ge mig mer skrivtid än vad som annars varit möjligt. Tack alla för att ni underlättade tillvaron!

Vägen har varit lång men många härliga ögonblick har passerat. Det allra viktigaste har dock skett utanför doktorandarbetet. Tillsammans med Hanna, min fru, har jag fått två fantastiska tjejer som sprutar av glädje och energi. Tack Hanna för att du stöttat och ställt upp alla dagar i veckan så att jag kunde slutföra detta arbete. Du hjälpte också till med de inledande fältförsöken – allt för att vi skulle få mer tid tillsammans. Maj och Signe, mina älsklingar, ni har fått mig att leva i nuet och tänka på mera *jordnära* saker under min lediga tid. Nu ska jag ge tillbaka av energi och glädje till er!