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Importance of dissolved organic carbon for transport of organic contaminants in groundwater

Betydelsen av löst organsikt kol för transport av organiska föroreningar i grundvatten

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Lisa Söderberg

ABSTRACT

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The need of understanding transport processes of contaminants in groundwater has grown along with the discovering of contamination of soil and groundwater due to industrialization. Mobility of an organic contaminant in the soil is affected by its partitioning to dissolved organic carbon, DOC. Partitioning of hydrophobic organic contaminants, HOCs, to DOC is described by the contaminant's K_{DOC} value. The effects of DOC on transport processes of organic contaminants with groundwater are still relatively unexplored even though some reviews have been carried out in this particular field of research. The aim of this thesis work was to investigate transport processes for the PAH phenanthrene and the phthalate Di(2-ethylhexyl) phthalate, DEHP, with DOC by constructing a transport model with the computer program FEFLOW 6.1. The thesis work was performed as part of an ongoing Research & Development project investigating alternative remediation techniques at Domsjö industrial site, located 2 km south of Örnsköldsvik.

Generally, the groundwater at the site was characterized by low phenanthrene and DEHP content together with high DOC content. In the sampling points with highest reported contaminant concentration also DOC was present in highest concentrations. During the performed literature study it was found that tabulated K_{DOC} values for phenanthrene was available but not for DEHP, which had to be calculated based on available K_{OC} and K_{OW} values. Five different modeling scenarios were developed:

1. Transport of phenanthrene with K_{DOC} minimum value.
2. Transport of phenanthrene with K_{DOC} maximum value.
3. Transport of phenanthrene with K_{DOC} median value.
4. Transport of DEHP with K_{DOC} calculated with K_{OC}.
5. Transport of DEHP with K_{DOC} calculated with K_{OW}.

Calculations of contaminant concentration in groundwater were made with an equation that requires both site and contaminant specific constants. These constants had to be estimated during this thesis work, which resulted in insecurities possibly affecting the model results. However, the minimum and the median value of K_{DOC} showed best modeled phenanthrene concentration after six years compared to measured values. Best result of modeled concentrations of DEHP was obtained with K_{DOC} calculated with K_{OC}. Correlation analysis of DOC and contaminants showed a significant correlation between DOC and phenanthrene at 99% confidence level, and between DOC and DEHP at 90% confidence level.

Keywords: modeling, FEFLOW, sorption, K_{DOC}, phenanthrene, DEHP

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REFERAT

Betydelsen av löst organsikt kol för transport av organiska föroreningar i grundvatten

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I takt med ökad kännedom om industriellt förorenade områden har det också blivit betydelsefullt att känna till de processer som påverkar transport av föroreningar med grundvattnet. Rörligheten av en hydrofobisk organisk förorening, HOC, påverkas av dess fördelning till löst organiskt kol, DOC, och beskrivs med fördelningskoefficienten K_{DOC}. Effekterna av DOC på föroreningstransporten är relativt okända trots att forskning har bedrivits inom området. Syftet med examensarbetet var att undersöka spridning av fenantren (ämnesklass PAH) och Di(2-etylhexyl)ftalat med DOC genom att konstruera en föroreningsspridningsmodell i datorprogrammet FEFLOW 6.1. Examensarbetet utfördes som del i ett pågående Forsknings & Utvecklingsprojekt med syfte att utreda en alternativ saneringsteknik för Domsjö industriområde, 2 km söder om Örnsköldsvik.

Generellt sett karaktäriserades grundvattnet på platsen av låg fenantren- och DEHP-halt tillsammans med hög DOC-halt. På samma ställen där föroreningarna förekom i högsta koncentration var också DOC-koncentrationen som högst. Vid genomförd litteraturstudie återfanns tabellerade K_{DOC}-värden endast för fenantren. K_{DOC} för DEHP saknades och fick beräknas med ekvationer baserat på förhållandet mellan K_{DOC} och K_{OC} respektive K_{OW}. Fem olika modelleringsscenarier utvecklades:

1. Spridning av fenantren med minsta tillgängliga K_{DOC}-värde.
2. Spridning av fenantren med högsta tillgängliga K_{DOC}-värde
3. Spridning av fenantren med median K_{DOC}-värde
4. Spridning av DEHP med K_{DOC} beräknat med $K_{OC.}$
5. Spridning av DEHP med K_{DOC} beräknat med $K_{OW.}$

Beräkning av föroreningarnas koncentration i grundvattnet gjordes med en ekvation som egentligen kräver både plats- och föroreningsspecifika konstanter. Då detta inte fanns att tillgå gjordes uppskattning av värdena vilket resulterar i osäkerheter som kan ha påverkan på modellerade resultat. De bästa modellerade koncentrationerna av fenantren efter sex års simulering jämfört med uppmätta koncentrationer uppnåddes med minsta och median-värde av K_{DOC}. Bästa modellerade koncentrationerna av DEHP gavs av K_{DOC} beräknat med K_{OC}. Korrelationstest med DOC och respektive förorening visade en signifikant korrelation mellan DOC och fenantren vid 99% konfidensnivå, och mellan DOC och DEHP vid 90% konfidensnivå.

Nyckelord: modellering, FEFLOW, adsorption, K_{DOC}, fenatren, DEHP

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PREFACE

This thesis work was performed as the final part of my Master's degree in Environmental and Water Engineering at Uppsala University. The thesis was made as part of phase II of a Research & Development project examining alternative environmental remediation techniques at active contaminated industrial sites in cooperation with Umeå University, Holmen AB, Tyréns, Sweco and MoRe Research. Supervisor was Martin Bergvall at Tyréns department of Geotechnical Engineering in Umeå and reviewer was Fritjof Fagerlund from the department of Earth Sciences, Air, Water and Landscape Sciences at Uppsala University.

I would like to take the opportunity to thank my supervisor Martin for helpful guidance and support during my thesis work. I am truly grateful for your patience and engagement in my work. I also would like to thank my reviewer Fritjof for valuable comments on thesis content.

Last but not least I would like to thank all of the staff members at the department of Geotechnical Engineering at Tyréns in Umeå who all have been very supportive and kind to me from day one of this thesis work.

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Lisa Söderberg

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POPULAR SCIENTIFIC SUMMARY

Importance of dissolved organic carbon for transport of organic contaminants in groundwater

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Legislation against emission of contaminants has not always been granted. In fact, legislation started at first in the 1960's when environmental and human health effects were proven to be a consequence of industrialization and the use of pesticides, such as PCB and DDT. By that time, contamination was already a problem. Organic contaminants are fat soluble substances stable to degradation, why they are often found in predators that are at the top of the food chain. They bio accumulates in fat tissues and biomagnifies in the food chain. Environmental effects of pollution are therefore often discovered far away from the source. One example is the sudden decrease of the sea eagle population in the 1960's. A lot indicates that release of PCB and DDT had affected the eagle's reproduction ability. PCB and DDT had biomagnified in the food chain causing fish eagles to be the most severely affected.

Organic contaminants are often spread by waters. Contaminants present in the soil may leach to groundwater and eventually recipients such as streams, lakes and coastal waters. To prevent large impact of polluting activity the European Parliament established The Water Framework Directive (2000/60/EC). All membership countries of the European Union are obliged to make sure that all lakes, streams and coastal waters have reached the main goal "Good status" by the year of 2015. One of the sub targets of the Directive is to reduce contaminant concentration in freshwaters. As a consequence of industrial contamination of land the Environmental Objective "A non-toxic environment" was developed by the Swedish Parliament. It states that man-made substances should harm neither human health nor the biodiversity. Concentration of man-made substances in the environment should be close to zero.

Organic contaminants have low water solubility and do not occur freely in water phase. Partition of organic contaminants is either to soil organic matter, SOM, or dissolved organic carbon, DOC, in soil pore water. SOM results from decomposition of litter and other dead organic matter in the soil. In contact with water SOM may dissolve and form DOC. Contaminants bound to SOM are likely to retain in the soil while contaminants bound to DOC is transported with groundwater flow. Need of understanding transport processes of organic contaminants with groundwater is therefore of crucial importance. In this thesis work a case study of contaminants spreading due to DOC was performed at Domsjö industrial site.

About 2 km south of Örnsköldsvik is Domsjö industrial site. Ever since the early 20th century industrial activities have been present in Domsjö. Today the main product produced in Domsjö is cellulose used in viscose fabric. Besides cellulose, lignin and bioethanol is also produced at the site. Due to the extensive industrial land use for more than 100 years Domsjö industrial site is contaminated with heavy metals and organic contaminants. A Research & Development project investigating alternative remediation techniques at the site was initiated in 2007 by former and present industrial operators. The thesis work was performed as part of the ongoing R&D project.

The aim of this thesis work was to investigate transport processes for the organic contaminants phenanthrene and Di(2-ethylhexyl) phthalate, DEHP, with DOC by constructing a transport model with FEFLOW computer modeling program. Computerized groundwater models able to predict groundwater properties are an essential and cost-efficient tool for prediction of groundwater flow and examination of risk assessments. Instead of performing expensive experiments in a laboratory, simulation of groundwater flow and effects of different remediation techniques can be tested inside the computer model.

Phenanthrene is a Polycyclic Aromatic Hydrocarbon, PAH, used as a component in dyestuffs as well as making explosives, pesticides and plastics. Phenanthrene is also present in creosote, a wood preservative used in coal tar. Like many PAHs phenanthrene is generated as a byproduct of incomplete combustion of organic material. It occurs both naturally in the environment and has anthropogenic sources. DEHP is a phthalate commonly used as plasticizer in PVC materials such as bottles, fabric coatings and medical plastics. Contradictory to phenanthrene, DEHP does not occur naturally in the environment. It is an industrial produced chemical which only has anthropogenic sources.

The content of phenanthrene and DEHP in the groundwater at Domsjö industrial site was low. Three out of ten analyzed samples of phenanthrene were below detection limit for phenanthrene. Five out of ten analyzed samples of DEHP were below detection limit for DEHP. All of the samples had concentration below guideline values. However, at the sampling points where contaminant concentration was highest also DOC concentration was highest. Generally, DOC content was high in all sampling points. A significant correlation was found between DOC and phenanthrene at 99% confidence level, and between DOC and DEHP at 90% confidence level.

DOC proved to be important for contaminant concentration in groundwater even though the relationship between modeled and measured contaminant concentration was not perfect. Calculations of contaminant concentration in groundwater were made with an equation that requires both site and contaminant specific constants. During this thesis work the constants had to be estimated which resulted in insecurities possibly affecting the model results. To show a more representative picture of reality, it is better to use measured constants as input to the model instead of estimated and tabulated.

Due to the persistency and toxicity of phenanthrene, DEHP and also other organic contaminants, prevention of contaminant transport is essential to avoid negative impacts on aquatic ecosystems. Clearly, DOC has an important role for transport of hydrophobic organic contaminants in the groundwater. By understanding these transport processes better, development of transport models and suitable remediation techniques is enhanced.

ABBREVIATIONS

C_s	Concentration of contaminant in soil
C_w	Concentration of contaminant in pore water
C_{w_mob}	Concentration of mobile contaminant
DEHP	Di(2-ethylhexyl) phthalate
DOC	Dissolved Organic Carbon
H	Henry’s law constant
HOC	Hydrophobic Organic Contaminant
K_d	Soil solution partitioning coefficient
K_{DOC}	Partitioning coefficient to DOC
K_{OC}	Partitioning coefficient to organic carbon
K_{OW}	Octanol-water partitioning coefficient
PAH	Polycyclic Aromatic Hydrocarbon
ρ_b	Bulk density
R&D	Research and Development
SOM	Soil Organic Matter
θ_a	Soil air content
θ_w	Soil water content

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1 INTRODUCTION

Contamination of land due to industrial activity began in the end of the 19th century when global industrialization took off. The environmental and human health effects, however, were not given any attention until the 1960's when environmental awareness increased over the world. At the same time responsibility for emissions and remediation of contaminated sites was legislated (Bernes, 1998). Spreading of contaminants from soil to recipients as groundwater and surface waters serve as potential risk of harming aquatic ecosystems and affecting water quality.

The Water Framework Directive (2000/60/EC) established by the European Parliament oblige all membership countries of the European Union to make sure that all lakes, streams, coastal waters and groundwater have reached the main goal "Good status" by 2015. One of the sub targets of the Directive is to reduce contaminant concentration in freshwaters (Swedish EPA, 2009a). To protect groundwater from contamination the European Parliament established Directive 2006/118/EC. Groundwater is the main source for drinking water in many countries and since groundwater represents as much as 90% of the base flow in all streams risk of contaminants spreading to receiving waters is high. Once groundwater have become contaminated, it is difficult to clean (European Union, 2007).

As a consequence of industrial contamination of land the Environmental Objective "A non-toxic environment" was developed by the Swedish Parliament. It states that man-made substances should harm neither human health nor the biodiversity. Concentration of man-made substances in the environment should be close to zero. The Swedish County Administrative Boards have estimated 50 000 contaminated sites in need of remediation in Sweden to reach the objective to the year of 2020 (Miljömål, 2012).

One of the contaminated sites in need of remediation is Domsjö industrial site located 2 km south of Örnsköldsvik in the County of Västernorrland. Ever since the early 20th century, industrial activities have been present in Domsjö. The very first activity included sulphite production (Domsjö Fabriker, 2013). Since then land use has changed from steam sawmill, chlor-alkali- and chlorate production to organic chemical industry and distillery (Sweco, 2008). Today the main product produced in Domsjö is cellulose used in viscose fabric. Besides cellulose, lignin and bioethanol is also produced at the site (Domsjö Fabriker, 2013). Because of the extensive industrial land use in more than 100 years Domsjö industrial site is contaminated with both heavy metals and organic contaminants (Sweco, 2008).

Since the industrial production at Domsjö takes place nearby the coastline there is high risk of contaminants spreading to the Örnsköldsvik Bay and eventually the Baltic Sea. Due to a water retention time of 25 years many of the toxic contaminants have time to bind to particles and finally sediment to the sea bottom where they can remain for longer periods of time (Bernes, 1998).

During the year of 2005 to 2006 the County Administrative Board of Västernorrland completed a MIFO (methodology for inventory of contaminated sites) Phase II investigation at Domsjö industrial site. According to this investigation Domsjö industrial site is classified as category 1, which means very high risk in terms of affecting human health and environment (County Administrative Board of Västernorrland, 2011). Thus Domsjö industrial site counts as one of Västernorrland County's most prioritized areas.

In 2007 former and present industrial operators initiated an immersed pilot study at the site. The pilot study included sampling of soil, sediments and groundwater. Also risk assessments and action programs were included. This was the start of an ongoing environmental investigation cooperated by the County Administrative Board of Västernorrland and former and present industrial operators. Later on in 2009, Umeå University together with Holmen AB, MoRe Research, Sweco and Tyréns started a Research and Development project called "Alternative environmental technology for contaminated sites with ongoing industries – a R&D project with focus on Domsjö industrial site in Örnsköldsvik". The R&D project aims to investigate and form alternative soil remediation techniques at active industrial sites. The project includes deepening knowledge of contaminant behavior in soil, modeling of groundwater flow and contaminant transport and development of remediation techniques at active industrial sites (Tysklind, 2011). Phase I of the R&D project ended in 2010, when phase II began.

A stationary groundwater flow model for part of the Domsjö industrial site was constructed in Processing MODFLOW (Pro 7.017) by Viktória Mikita (University of Miskolc, Hungary) during phase I of the R&D project (Tysklind, 2011). Also in phase I, a transport model for seven organic contaminants was constructed in Processing MODFLOW (Pro 8.0) with MT3DMS interface. Contaminants included DDT, DDD, DDE, trichlorophenols, 2-monochlorophenols, aliphatics C10-C12 and organic acids C8-C10. The transport model focused on mapping contaminant distribution. Leaching of contaminants from soil to groundwater was based on groundwater recharge and K_d values (Tysklind, 2011). Transport of contaminants with dissolved organic carbon, DOC, was not taken into account.

Frankki (2006) established in her doctoral thesis that the mobility of hydrophobic organic contaminants, HOCs, is controlled by its partitioning to DOC. Partitioning coefficient to DOC is called K_{DOC}. With the help of K_{DOC}, concentration of mobile contaminants can be calculated. Best approximation of contaminant distribution with DOC is achieved by measured K_{DOC} values from soil at the actual site (Burkhard, 2000). Since this cost both time and money, evaluation of modeling contaminant transport with calculated K_{DOC} values is clearly of interest.

1.1 OBJECTIVE

The main objective of this thesis work was to extend the use of the previously mentioned transport model by investigating importance of DOC for transport of organic contaminants in groundwater. Since earlier research has shown correlation of spreading of organic contaminants with DOC, the aim of this thesis was to further investigate this relationship for contaminants phenanthrene and DEHP.

Specific objectives included:

- Formulate a model accounting for the influence of DOC (based on K_{DOC} values) on the spreading of phenanthrene and DEHP in groundwater.
- Evaluate the feasibility of modeling the spreading of DEHP with calculated K_{DOC} values (not tabulated as for phenanthrene).
- Evaluate correlations between concentrations of phenanthrene and DEHP with DOC.

To be able to construct a transport model, it is essential to have a working groundwater flow model as background. Since the groundwater flow model constructed in Phase I of the R&D

project only included parts of the Domsjö industrial site, a new model had to be made, including the entire site. The new groundwater flow model was constructed in computer program FEFLOW 6.1 by Martin Bervall at Tyréns.

1.1.1 Delimitations

Due to lack of time the organic contaminants discussed in this thesis are limited to only include phenanthrene and DEHP even though many other organic contaminants are present at the site. Phenanthrene and DEHP have different physical properties, such as diverse K_{OC} and K_{OW} values and are therefore interesting to evaluate from a mobility perspective. There are available measured K_{DOC} values for phenanthrene while none was available for DEHP. K_{DOC} for DEHP had to be calculated with an equation recommended by Swedish EPA (2009b) and Burkhard (2000) for organic contaminants.

The studied area of Domsjö industrial site investigated in this thesis work is delimited to the areas assumed to be worst contaminated by phenanthrene and DEHP. These are the areas closest to the shore line towards Örnsköldsvik Bay.

The limited time available for the thesis work made calibration of the groundwater flow model, used as background model for the constructed transport model, not completely reached before implementation of the transport model. Nonetheless, the groundwater model was considered to be sufficiently calibrated before implemented as background for the transport model. Validation of both groundwater flow model and transport model could not be made due to lack of data.

2 SITE DESCRIPTION

Domsjö industrial site covers a surface area of totally 0.92 km^2. The site is divided into three main areas: the Western area, the Cistern area and the Treetex area. Each main area is divided into subareas based on former and present land use. Subareas are named V1-V22 for the Western area and C1-C11 for the Cistern area. This thesis work focuses mainly on the Cistern area. However, to fully understand groundwater flow paths of the Cistern area the Western area had also to be investigated.

The Western area is the westernmost area at the site. It borders River Moälven in the south and the Cistern area in the east. The Cistern area borders the Western area in the west, River Moälven in the south, the Örnsköldsvik Bay in the east and the Treetex area in the north (Figure 1) (Sweco, 2008).

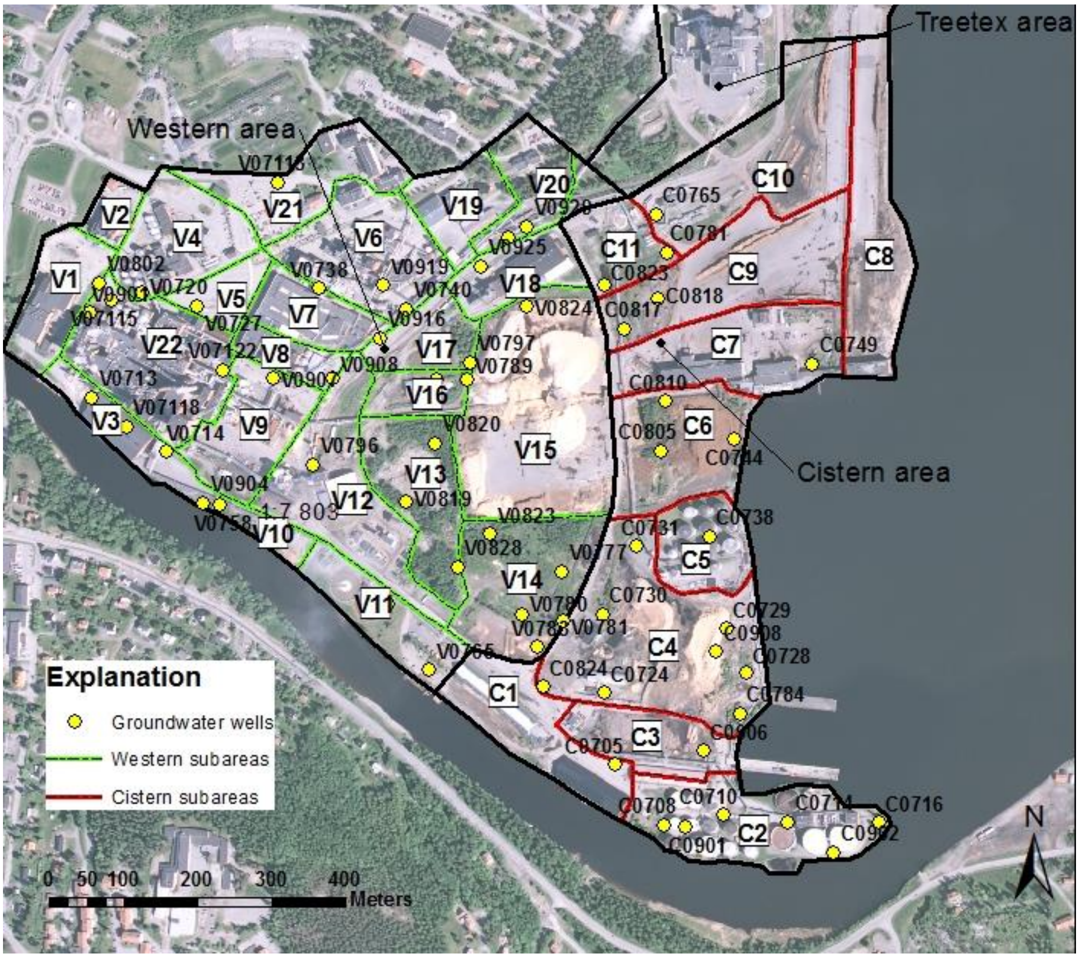


Figure 1. Domsjö industrial site has been divided into three main areas represented by black polygons: the Western area, the Cistern area and the Treetx area. Subareas within the Western area are named V1-V22 divided in the figure by green lines. Subareas within the Cistern area are named C1-C11, here divided by red lines. Groundwater wells are represented by yellow circles.

The Western area consists partly of sediment filling from River Moälven covering its south end. In the northeast of the Western area lies most of the buildings and factories present at Domsjö industrial site. Previous land use of the Western area included sulphite pulp-, chlor-alkali-, chlorate-, and organic chemical production. Industrial production today is mainly ethanol and cellulose derivatives. There is also a biorefinery in the Western area that produces fuel from biomass (Sweco, 2008).

Parts of the Cistern area were previously covered with sea water but has, during the last century, been filled with industrial residues and wastes. Other parts served as storage and chemical harbour. Today the area serves as (as its name implies) cistern area, harbour and biopurification area (Sweco, 2008).

2.1 CONTAMINATION SITUATION

In the pilot study from 2008, ten out of the 22 subareas in the Western area were classified as "very high risk" of affecting human health and environment, the highest risk classification. Analysis of soil samples showed that 25% had contaminant concentration exceeding the Swedish environmental protection agency's (Swedish EPA's) guideline values for less sensitive land use. Dominating this contamination was mercury. Various organic contaminants like phthalates, dioxins, pesticides and organic acids were also found in the soil. The groundwater had lower content of contaminants (Sweco, 2008).

Six out of the eleven subareas in the Cistern area were classified as "very high risk" of affecting human health and environment. According to the pilot study (Sweco, 2008) 35-40% of the soil samples had contaminant concentration exceeding Swedish EPA's guideline values for less sensitive land use. Metals like arsenic, mercury and lead were found in the soil. Also found in the soil was organic contaminants like phthalates, organic acids and petroleum products. The substances were present also in groundwater. Risk of contaminants spreading to River Moälven and the Örnsköldsvik Bay was considered to be high (Sweco, 2008).

Screening analyzes of soil and groundwater samples with GC-MS performed on phthalates, substituted benzenes, naphthalene and phenols in a few sampling points showed high content of the phthalate DEHP and the PAH phenanthrene. Phenanthrene was present in the soil at concentration of 10-20 mg/kg in points V0779 and V0780. DEHP concentration in the soil was 40 mg/kg at its highest present in point C0708. Production, storage, degradation products, leakage and spill of the contaminants at the site are the believed sources for both phenanthrene and DEHP (Sweco, 2008).

3 THEORY

3.1 GROUNDWATER FLOW

The outline of an aquifer in a watershed is determined by the groundwater divides which in turn are determined by the groundwater surface. In most cases groundwater surface follows topography as in Figure 2. The recharge areas are at the highlands while discharge areas lies in the lowlands. The regional flow, at large depths, is smaller than the local flow at more shallow depths (Grip & Rodhe, 1994).

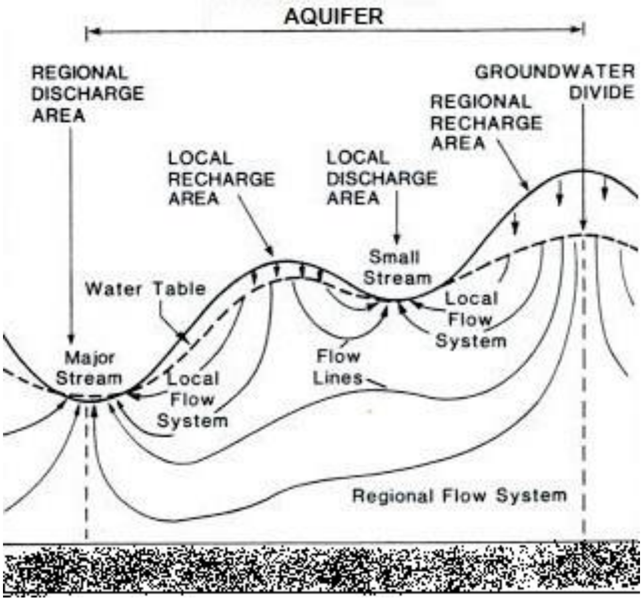


Figure 2. Groundwater flow direction in a cross sectional landscape. The size of the aquifer is determined by its groundwater divides. To the left hand side groundwater divide is in the middle of the major stream. To the right hand side groundwater divide is at the highest point of the hill (and groundwater surface). Precipitation contributes to groundwater recharge at the hills. Discharge areas are in the valleys (After Tóth, 1963).

3.1.1 Driving forces of groundwater flow

Groundwater flow is driven by the gradient of hydraulic head. The flow follows the groundwater surface and streams from high to low hydraulic head. The Darcy equation describes this relationship (equation 1). The specific discharge (Darcy velocity), q, is directly proportional to the hydraulic gradient ∇h, which describes how the hydraulic head changes from one point to another. Also affecting groundwater flow is the hydraulic conductivity, K, i.e. the ability of the soil to conduct water (Grip & Rodhe, 1994).

$$\bar{q} = -\bar{K}\nabla h \qquad (1)$$

where q is the specific discharge (Darcy velocity) [m/s], K is the hydraulic conductivity of the soil [m/s] and ∇h is the hydraulic gradient [m/m]. The flow can be in either direction (x, y or z). However, the horizontal component is usually the largest for saturated groundwater flow. The hydraulic head, h, can be measured in the field as the height of the groundwater table in a groundwater well. Hydraulic conductivity can also be measured in the field by performing e.g. multi-well pumping tests or single-well slug tests (Grip & Rodhe, 1994).

3.1.2 Continuity equation

Conservation of mass states that mass is conserved in a closed system (Anderson & Woessner, 1992). The outflow minus inflow of water through a representative elementary volume, REV, with the dimension of Δx Δy Δz equals change, or release, in storage:

release storage = outflow – inflow

Assuming constant density, the change in storage can be described as follows (Anderson & Woessner, 1992):

$$release\ storage = \left(\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z}\right) \Delta x \Delta y \Delta z \qquad (2)$$

Change in storage may also be referred to as specific storage S_s (volume of water released from storage per unit change in head and unit volume of the aquifer), equation 3. When the change in head is negative, the release is positive and water is released from the REV (Andersson & Woessner, 1992).

$$S_s = -\frac{\Delta V}{\Delta h \Delta x \Delta y \Delta z} \qquad (3)$$

The rate at which change in storage alters is in turn explained by equation 4.

$$\frac{\Delta V}{\Delta t} = -S_s \frac{\Delta h}{\Delta t} \Delta x \Delta y \Delta z \qquad (4)$$

The continuity equation (equation 5) is obtained by combining equation 2 and 4 (Anderson & Woessner, 1992).

$$\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z} = -S_s \qquad (5)$$

3.1.3 Governing equation of groundwater flow

Since groundwater flow is difficult to measure in reality, equation 5 has to be rewritten. By combining Darcy equation (equation 1) and continuity equation (equation 5) specific discharge q can be replaced by hydraulic conductivity and hydraulic head. The result forms the governing equation (equation 6) for transient groundwater flow in a saturated, heterogeneous and anisotropic media (Anderson & Woessner, 1992).

$$\frac{\partial}{\partial x}\left(K_x \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial h}{\partial z}\right) = S_s \frac{\partial h}{\partial t} \qquad (6)$$

For stationary conditions in anisotropic media $\frac{\partial h}{\partial t} = 0$ and equation 6 can be rewritten as equation 7 (Larsson, 2003).

$$\frac{\partial}{\partial x}\left(K_x \frac{\partial h}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y \frac{\partial h}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z \frac{\partial h}{\partial z}\right) = 0 \qquad (7)$$

3.1.4 Transport of solutes

Advection, sorption, dispersion and diffusion govern transport mechanisms of dissolved substances in groundwater. Transport of substances only with groundwater flow is called advective transport (Larsson, 2003). The average groundwater flow velocity affecting the advective transport in the soil is determined by equation 8 (Kresic, 2007).

$$v = \frac{K}{n_{ef}} \cdot \nabla h \qquad (8)$$

where v is the linear groundwater velocity [m/s], K is the hydraulic conductivity [m/s], ∇h is the hydraulic gradient [m/m] and n_{ef} is the effective porosity of the soil [-]. Equation 8 is based on the assumption that the hydraulic conductivity, hydraulic gradient and effective porosity all are constant and also that the contaminant is not retarded in the soil (Kresic, 2007).

However, since pore size and tortuosity varies throughout the soil, some molecules will move faster than the average molecules. This is called hydrodynamic dispersion, D_x. Hydrodynamic dispersion is the sum of mechanical dispersion ($\alpha_x v_x$) and diffusion (D_e), described by equation 9. As a result of velocity differences between molecules in the water, mechanical dispersion occurs either in a pore scale level or between pores (Figure 3). Diffusion is, in this context, a slow process that only has an importance if the groundwater flow is slow. It is driven by a concentration gradient and will continue as long as there is a concentration gradient (Kresic, 2007).

$$D_x = \alpha_x v_x + D_e \tag{9}$$

where D_x is the hydrodynamic dispersion [m^2/s], α_x is the longitudinal dispersivity [m], v_x is the linear groundwater velocity in [m/s] and D_e is the effective diffusion (Kresic, 2007).

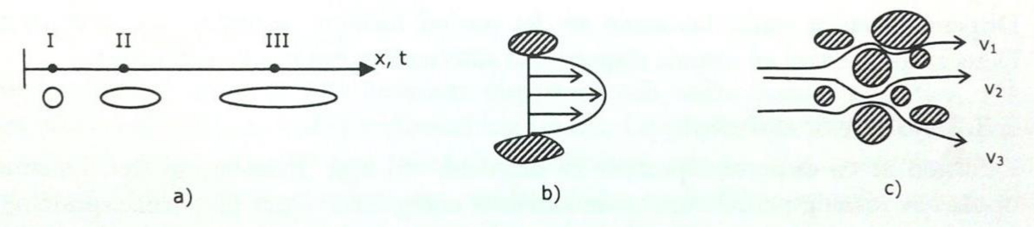


Figure 3. a) Conceptual interpretation of a contaminant spreading in the soil with time and space. Some of the molecules will move faster and/or slower than the average molecules resulting in an elongated plume. b) Mechanical dispersion on a pore scale level. Molecules transported in the middle of the pore will travel with a faster average velocity than the ones transported close to the soil due to friction. c) Mechanical dispersion between the pores due to soil heterogeneity and tortuosity causing molecules to achieve different velocities (with permission from Larsson, 2003).

The most important factors affecting transport of contaminants is groundwater flow, sources of the studied contaminants and transport processes of each contaminant (Swedish EPA, 2007a). Due to the contaminant properties such as water solubility and density, the contaminants will either be transported with water flow (water soluble contaminants such as acids, bases and salts), lie on top of the groundwater table and transported only with shallow water (lighter organic contaminants such as petrol and oil) or end up at the bottom of the groundwater table (heavier organic contaminants such as chlorinated solvents) (Swedish EPA, 2007a).

Most of the spreading of HOCs during early stages of contamination is by water flow as an advective-dispersive process. Contaminants bound to SOM are likely to retain in the soil while contaminants bound to DOC are mobile and travel with water as an advective-dispersive process (Persson, personal communication, 2013).

3.2 SOIL ORGANIC MATTER

Decomposition of litter and other dead organic matter in the soil results in soil organic matter, SOM (Persson, 2007). The source of organic matter highly affects the composition of SOM. For example, organic matter from microbial dead organic matter, such as algae and bacteria, tends to have low phenolic and aromatic carbon content. At the same time it consists of great amount nitrogen. Organic matter from higher plants such as trees or grass has larger amount of phenolic and aromatic carbon, and low nitrogen content (US Geological Survey, 2013a).

SOM includes both hydrophobic and polar structures. The hydrophobic part comes from aliphatic and aromatic structures forming a hydrophobic skeleton. Functional groups in SOM like hydroxyl, carboxyl and amino groups add a portion of polarity to the material. Also groups containing phosphorus and sulphur play an important role for the partial polarity of

SOM. SOM also constitutes of black carbon, BC, formed by incomplete combustion processes (Persson, 2007). BC is planar in its composition and have none or low amount of polar/hydrophilic functional groups.

In water, SOM may dissolve and form DOC. Ionic strength, pH and composition of adsorbed major cations determine the amount of SOM released to pore water as DOC. DOC is often defined by its size such as passing a filter with defined pore size of 0.45 μm (Frankki, 2006). Due to the polarity of DOC and the capability to form hydrogen bonds it is mobile in water (Persson, personal communication, 2013).

3.2.1 Partitioning of HOCs to SOM and DOM

In the soil HOCs are distributed to two separate pools: immobile SOM and mobile DOC. SOM has a larger hydrophobic structure compared to DOC. For sorption of HOCs to SOM, hydrophobic interaction is the most important mechanism (Persson, personal communication, 2013). Driving force of hydrophobic interaction is entropy differences between polar water phase and hydrophobic SOM (Frankki, 2006). Since SOM is more hydrophobic than DOC, hydrophobic interaction of HOCs with SOM is stronger than with DOC. Hydrophobicity of HOCs depends on the compounds size, planar constitution and lack of functional groups (Persson, personal communication, 2013). Presence of BC in SOM also increases sorption of HOCs. Especially HOCs with a planar structure have been proven to adsorb to BC (Persson, 2007). More polar contaminants adsorb in greater extent to DOC (Persson, personal communication, 2013).

3.3 MOBILITY OF ORGANIC CONTAMINANTS IN GROUNDWATER

Burkhard (2000) investigated the relationship between K_{DOC} values and K_{OW} values based upon 73 references of measured K_{DOC} data. The result showed a predictive relationship of K_{DOC} as a function of K_{OW} as shown in equation 10. A relationship between K_{DOC} and K_{OC} (equation 12) can also be derived from equation 11, showing K_{OC} as a function of K_{OW}.

$$K_{DOC} = 0.08 \cdot K_{OW} \qquad (10)$$

$$K_{OC} = 0.33 \cdot K_{OW} \qquad (11)$$

$$K_{DOC} = 0.24 \cdot K_{OC} \qquad (12)$$

where K_{DOC} is the contaminant partitioning coefficient to dissolved organic carbon [L/kg], K_{OW} is the octanol/water partitioning coefficient [L/kg] and K_{OC} is the partitioning coefficient to organic carbon [L/kg].

Equation 10 was developed based upon naturally occurring DOC. Another relationship for Aldrich humic acid (laboratory produced humic acid) was also found by Burkhard (2000) but will not be discussed further in this thesis. The 95% confidence interval of equation 10 has a factor of 20, which means that calculated K_{DOC} values may be as much as 20 times smaller or 20 times higher than the actual value. Equation 10 gives an average value of K_{DOC}. As a consequence, there might be large uncertainties in K_{DOC} values resulting from equation 10. The origin of DOC in the 73 references used to create equation 10 varies between soil, surface water and sediment. Origin of DOC affects the difference in structure and composition of the DOC molecules which in turn have high effect on the K_{DOC} values (Burkhard, 2000).

Swedish EPA (2009b) published a report that aims to serve as a guide when calculating guideline values in contaminated soils. The method described in the report uses K_{DOC} values to calculate organic contaminant concentration in groundwater. The concentration of mobile contaminant is calculated with equation 13, hereafter called mobility equation.

$$C_{w\_mob} = C_w(1 + K_{DOC}DOC) \tag{13}$$

Where C_{w_mob} is the concentration of mobile contaminant [mg/L], C_w is the concentration of contaminant in pore water [mg/L] and DOC is the amount of dissolved organic carbon [kg/L].

C_w is, in turn, calculated based on equation 14.

$$C_w = C_s \Big/ \left[K_d + \frac{(\theta_w(1+K_{DOC}DOC)+\theta_a H)}{\rho_b}\right] \tag{14}$$

Where C_s is the concentration of a contaminant in the soil [mg/kg dry weight], θ_w is the soil water content [dm^3 water/dm^3 soil], K_d is the contaminant distribution coefficient between soil and water [L/kg], θ_a is the soil air content [dm^3 air/dm^3 soil], H is Henry's constant [$atm \cdot m^3/mol$] and ρ_b is bulk density [kg/dm^3].

3.4 STUDIED ORGANIC CONTAMINANTS

The contaminants studied in this thesis work, phenanthrene and DEHP, are persistent organic contaminants which means they are stabile to degradation in the environment and thus long-lived (Bernes, 1998). To describe an organic contaminant's water solubility, the contaminant's octanol/water partitioning coefficient is used (K_{OW}). The ratio of the chemicals's concentration in n-octanol compared to its concentration in water defines K_{OW} (US Geological Survey, 2013b). Another partitioning coefficient used for organic contaminants is K_{OC}, describing the contaminant's partitioning to organic carbon in relation to water. To describe the contaminant's partitioning to DOC in relation to water, K_{DOC} is used (Swedish EPA, 2009b). Both phenanthrene and DEHP have K_{OW} values > 1000 making them very hydrophobic (Chiou, 2002). Their physical properties are described in Table 1 where three different K_{DOC} values for phenanthrene and two different K_{DOC} values for DEHP are shown.

Table 1. Physical properties of phenanthrene and DEHP.

Physical property	Phenanthrene	DEHP
CAS number	85-01-08	117-81-7
Class	PAH	Phthalate
Molecular weight [g/mol]	178.2	390.5
Dissociation constant, pKa	>15[a]	Unavailable
Log K_{OW} [log L/kg]	4.57[b]	7.137[c]
Log K_{OC} [log L/kg]	4.36[b]	5.0[d]
Log K_{DOC} max [log L/kg]	3.91[e]	-
Log K_{DOC} min [log L/kg]	6.50[e]	-
Log K_{DOC} median [log L/kg]	4.51[e]	-
Log K_{DOC} from K_{OC} [log L/kg]	-	6.04
Log K_{DOC} from K_{OW} [log L/kg]	-	4.38

[a] Christensen et al., 1975.

[b] Karickhoff et al., 1979.

[c] Brooke et al., 1990.

[d] Neely & Blau, 1985.
[e] Burkhard, 2000.

Guideline values for contaminants differ depending on land use and in what matrix the contaminants are present (soil, surface water or groundwater). The Dutch National Institute for Public Health and Environment, RIVM, has developed guideline values for heavy metals and organic contaminants in soil and waters. Two commonly used guideline values are SRC_{eco} (ecotoxicological Serious Risk Concentration) and MPC (Maximum Permissible Concentration) (RIVM, 2001). The SRC_{eco} value is the expected concentration at which 50% of the species or processes in a population suffer no damage by a contaminant. MPC represents a concentration at which 95% of the species or processes in a population should be protected from damage by a contaminant. Guideline values of phenathrene and DEHP are described in Table 2. Swedish guideline values for DEHP could not be found. Since the Swedish guideline values for phenanthrene are similar to the Dutch guideline values, only the Dutch guideline values are given here.

Table 2. Guideline values of phenanthrene and DEHP.

Type of guideline value	**Phenantrene**	**DEHP**
Drinking water (1% of Tolerable Daily Intake) [µg/l]	None available	8.0[a]
SRC_{eco} in soil [mg/kg]	31[b]	69[b]
MPC in soil [mg/kg]	3.3[b]	6.9[b]
SRC_{eco} in surface water [µg/l]	30[b]	5.0[b]
MPC in surface water [µg/l]	3.2[b]	0.5[b]
SRC_{eco} in groundwater [µg/l]	30[b]	5.0[b]

[a] WHO, 2003.
[b] RIVM report 711701 020, 2001.

The European Parliament established in the year of 2001 a list of prioritized substances that serves as a risk to the aquatic environment according to the Water Framework Directive (2000/60/EC). Amongst the prioritized substances is DEHP. The prioritized substances will, together with other water related parameters, form the basis of the Swedish Water Authorities decision about status for the water (Swedish EPA, 2009a).

3.4.1 Phenanthrene

Phenanthrene is a PAH that is used in dyestuffs and when making explosives, pesticides and plastics. Besides this, phenanthrene is also present in creosote, a wood preservative used in coal tar. Like many PAHs phenanthrene is generated as a byproduct of incomplete combustion of organic material. It occurs both naturally in the environment and has anthropogenic sources (USA EPA, 2012). Phenanthrene consists of three fused benzene rings (Figure 4).

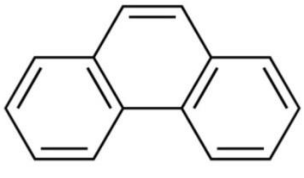


Figure 4. Structural formula of phenanthrene consistent of three fused benzene rings.

Exposure to phenanthrene can occur in several ways: dermal exposure through contaminated soil, inhalation of contaminated air or by ingestion of food (especially food that has been grilled or charred) that contains the contaminant. Because phenanthrene is a byproduct of incomplete combustion of fuel, hazardous waste and is present in tobacco smoke exposure through inhalation of contaminated air is the most common way of exposure (USA EPA, 2012).

Aerobic biodegradation of phenanthrene performed in laboratory studies with perfect conditions regarding temperature and unlimited nutrient supply shows a fast degradation rate (Hazardous Substances Data Bank, 2013). Although living organisms may metabolize PAHs quite fast PAHs can survive in aquatic environments for longer periods of time by binding to sediments (Bernes, 1998).

Not many studies have been made on human health effects of phenanthrene specifically. Studies made with laboratory animals on exposure of PAHs with higher molecular weight than phenanthrene shows that they can cause cancer. Phenanthrene is included in Swedish EPA's group of 16 prioritized PAHs, classified due to their toxicological and carcinogenic character (Nilsson, 2009).

3.4.2 DEHP

Di(2-ethylhexyl) phthalate, or DEHP, is a phthalate commonly used as plasticizer in PVC materials such as bottles, fabric coatings and medical plastics. DEHP does not occur naturally in the environment. It is an industrial produced chemical which only has anthropogenic sources (Montgomery, 2007). The DEHP molecule is a large molecule constituent of the typical phtalathe structure with ethylhexyl chains connected to the single bonded oxygen atoms (Figure 5).

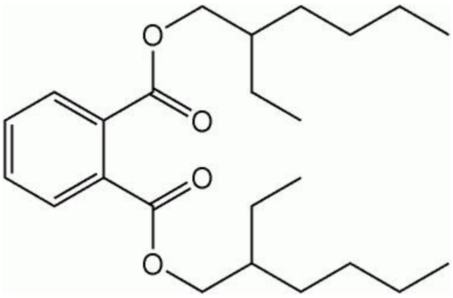


Figure 5. Structural formula of the DEHP molecule.

Even though the use of DEHP in Sweden has decreased it is still common in the environment, especially as a point source close to landfills, due to its ability to bind to sediments and high bio accumulation factor (Loh & Ovuka, 2005).

Humans get exposed to DEHP either by inhalation of contaminated air, ingestion of food that contains the contaminant (mostly food with high fat content and milk products) or by dermal exposure and intravenous treatment. Due to the extensive use of DEHP as a plasticizer in medical products hospital patients are likely to be exposed when getting blood transfusions or having similar treatments. Also people working with manufacturing of PVCs are likely to be exposed by inhalation of air containing DEHP aerosols (IARC, 2000).

Phthalates in general have been found to be metabolized quite fast by vertebrates (Bernes, 1998). In the soil, however, DEHP adsorbs to organic matter making it unavailable for biotic degradation. Biodegradation seems to be dependent of oxygen because it is faster in aerobic aquatic environments. Experiments have shown DEHP to be persistent in anaerobic environments, such as groundwater and sediments (Swedish EPA, 2007b). DEHP also bio accumulates in aquatic organisms. In air DEHP may occur both as gas and bound to particles (Hazardous Substances Data Bank, 2013). Particle bound DEHP may travel long distances and is released to the ground and water by wet and dry deposition (IARC, 2000).

The health effects from DEHP exposure were brought to the surface at first in the 1970's when scientists discovered traces of DEHP in blood from blood bags containing PVC plastics. Later DEHP was found in human organs like lungs, spleen and liver in patients receiving blood from blood transfusions. DEHP has been proven to be carcinogenic to laboratory animals but not to humans. It has also been proven to cause reproductive damages in mice and rats (IARC, 2000). DEHP has been classified as reproduction toxic, category 2, by the Swedish Chemicals Agency which means it may cause reduced fertility and birth defects (KIFS 2004:7). After 1999 the use of DEHP in children's toys is limited (Hullberg & Hedlund, 2008).

3.5 GROUNDWATER MODELING

3.5.1 Conceptual model

When constructing a groundwater model the most important step is to make a conceptual model based upon the properties of the area of interest (Kresic, 2007). The conceptual model represents a simplified picture of reality. It should describe the relationship between groundwater conditions and hydrology, geology and topography. To make this possible, information of water balance such as precipitation, evapotranspiration, infiltration and groundwater recharge is needed. Also soil type, distance to impermeable rock and topography data need to be implemented in the conceptual model (Knutsson & Morfeldt, 2002). The conceptual model support the knowledge needed to solve equations mathematically with help of a computer program (Kresic, 2007).

3.5.2 Numeric model

Mathematical groundwater models can be either analytical or numerical. Analytical models solve only one equation at a time while numerical models use algorithms to solve a system of equations. The watershed is divided into smaller areas, cells, and the equations of each cell are calculated iteratively with a numerical method (Kresic, 2007). The finite difference and the finite element method are two common numerical methods used to solve equations in a groundwater model. Generally, finite difference models are easier to use and require less input data while finite element models use more complex equations but also better estimates in situations where the boundary conditions are irregularly shaped (Anderson & Woessner, 1992). The numerical model used in this thesis work applies the finite element method when solving equations, and therefore only this method will be discussed from here.

When constructing a finite element model, the area to be studied is assigned a mesh. Each element (cell) in the mesh is then associated with a node (Figure 6). The nodes are in the cell vertices. When calculating for example the hydraulic head of the area calculations are made at each node. Interpolation of functions makes the variation of head between the nodes defined (Anderson & Woessner, 1992). Model process variables like initial conditions of hydraulic head and fluid flow and also model boundary conditions are defined at the nodes. Other variables of material properties like hydraulic conductivity, porosity and dispersivity are defined within the cells (DHI-WASY GmbH, 2012).

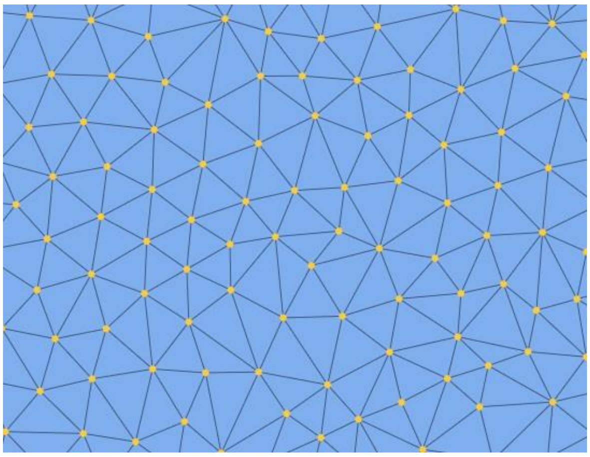


Figure 6. Finite element mesh with nodes in the cell vertices, here represented by a yellow dot.

With the finite element method, the cell shape of the watershed is either rectangular or triangular if the model is in two dimensions. In a three dimensional model the cell shapes can be in the form of prisms, tetrahedrons or hexahedrons. Soil and groundwater properties of all cells do not have to be constant when using the finite element method which means it is suitable when modeling areas with a heterogeneous character (Knutsson & Morfeldt, 2002).

To ensure that a constructed groundwater flow model is able to represent reality, for example calculate hydraulic heads that correspond to measured values of hydraulic head at the studied site, the model has to be calibrated (Anderson & Woessner, 1992). The calibration process can be executed manually as a trial-and-error process by changing model parameters until the model sufficiently enough represents measured values, or may be automated for certain parameters and ranges. The process includes changing of parameter values, boundary conditions and stresses. Estimated parameters that do not result from measurements at the actual site should be in focus during calibration. The user should be more cautious when changing measured parameters (Kresic, 2007). Before calibration starts an error range, in which model errors may be accepted, is set to avoid over-calibration of the model (Anderson & Woessner, 1992).

One way of evaluating model predictability is by calculating the model residual for an output variable. The mean absolute error, MAE, calculates the absolute value of the model residual as in equation 15 (Anderson & Woessner, 1992).

$$MAE = \frac{1}{n}\sum_{i=1}^{n}|h_m - h_s| \qquad (15)$$

where n is the sample size, h_m is measured hydraulic head and h_s is simulated hydraulic head.

3.5.3 FEFLOW 6.1

The computer program used in this thesis work to model groundwater flow and contaminant transport was FEFLOW 6.1. In FEFLOW a supermesh is designed containing the important geometrical information needed to construct the finite element mesh in a later stage. Depending on model use, the supermesh may be simple and contain one polygon representing the outer boundary of the model. It may also be more complicated containing several polygons, polylines and points describing subareas, river boundaries and wells inside the model area (DHI-WASY GmbH, 2012).

A precise design of the finite element mesh will ease numerical problems that otherwise may arise when running model simulation. In FEFLOW the user is given the opportunity to refine the mesh in local areas of interest (DHI-WASY GmbH, 2012).

When calculating groundwater flow in a saturated media FEFLOW uses the governing equation of groundwater flow (equation 6) - a combination of the Darcy equation and equation of continuity. In this thesis work the groundwater flow model is stationary and equation 7 is applied for calculations of groundwater flow. Transport of solutes is assumed to be an advective-dispersive process (DHI-WASY GmbH, 2012).

4 MATERIALS AND METHODS

The idea of the method was to construct a contaminant transport model in FEFLOW 6.1 with a working model for groundwater flow as background. Once the groundwater flow model was constructed the contaminant transport model was added to the groundwater flow model for simulation of contaminant transport. How this was done is described more closely in the following sections. Calibration of the background model for groundwater flow was not finished before this thesis work started. Calibration of the transport model with measured contaminant concentrations could, however, be made.

4.1 MAPS

The ortophoto used to create all maps of Domsjö industrial site was received from Läntmäteriet through the database Digital Maps, Swedish University of Agricultural Sciences. Coordinate system was in plane RT 90 2.5 gon V and height reference system RH70. To fit with previous measurement of groundwater levels in Domsjö local height reference system -2.76 m was subtracted from heights in RH70. Pretreatment of data was performed in ArcMap 10.1 with 3D Analyst Tool.

4.2 GROUNDWATER SAMPLING

In 2007 Sweco installed 74 groundwater wells at the Domsjö industrial site. During the field study performed in this thesis work, it was found that only 28 of the groundwater pipes were left and had satisfactory inflow rate for sampling of groundwater. More than half of the originally installed 74 groundwater pipes were either destroyed or found to have too low supply inflow rate for sampling.

For analysis of PAHs and phthalates in groundwater, samples were collected from 10 groundwater wells at the site. In each well 2 L of groundwater were collected and put in 1 L glass bottles. Also samples for analysis of DOC concentration in groundwater were collected from 19 groundwater wells and put in 150 mL plastic bottles. The locations of the groundwater wells used for sampling are shown in Figure 7.

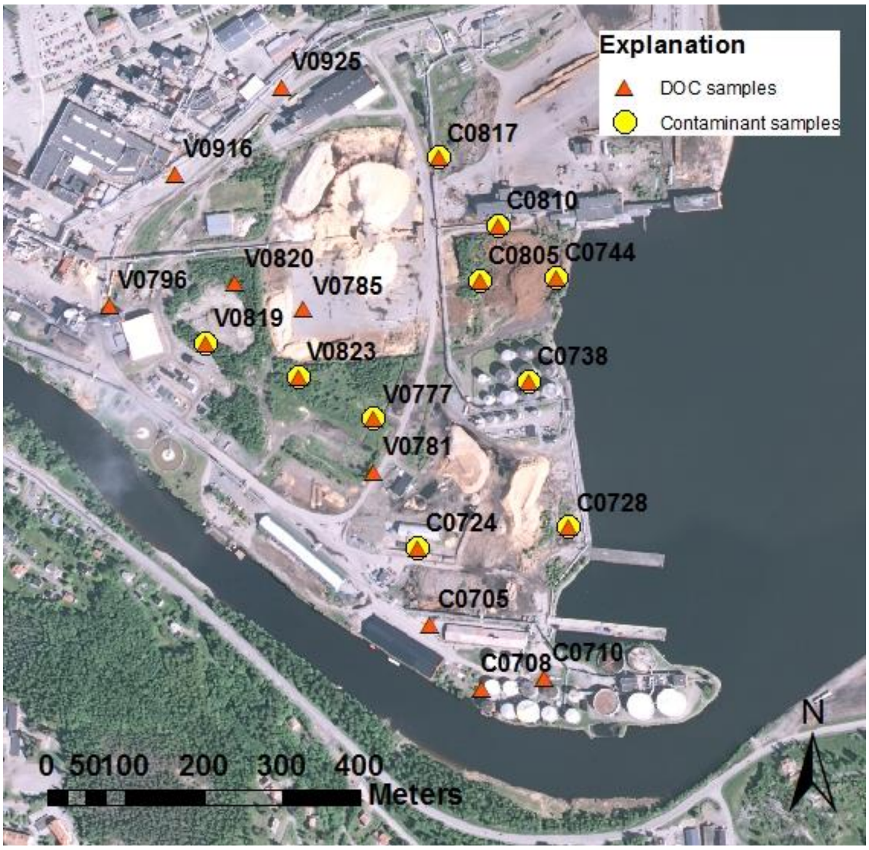


Figure 7. Locations of the groundwater wells used for sampling at the Domsjö industrial site. Yellow circles represent sampling of PAHs and phthalates. Orange triangles represents sampling of DOC.

All groundwater samples were sent to ALS Laboratory Group in Täby who performed analysis on PAH, phthalate and DOC content in the samples.

4.3 CORRELATION TEST

To determine whether two variables covariate, the correlation between them can be investigated. Correlation of variables can be either positive or negative. A positive correlation implies that when the value of the independent variable increases, the dependent variable value also increases (Borg & Westerlund, 2012).

To test the significance of a covariance the probability value, p-value, can be calculated. By comparing the p-value to the significance level α (the probability of outcome in the critical area even though H_0 is confirmed) H_0 is either confirmed or rejected. If p-value $< \alpha$ H_0 is rejected (Borg & Westerlund, 2012).

For statistical analysis of sampled groundwater data the computer program R was used. In R correlation coefficient R and p-value were calculated to test the significance of the possible correlation between the contaminants and DOC. To achieve a linear relationship between the studied variables both of them had to be logarithmic before analysis could be made. The significance level α was set to 0.05.

4.4 GROUNDWATER FLOW MODEL

A prerequisite for construction of a contaminant transport model is to have a working groundwater flow model as background. The groundwater flow model constructed in phase I of the R&D project was made in computer program MODFLOW and included only subarea C6. During this thesis work construction of a new groundwater flow model, including the entire Domsjö industrial site, was made in FEFLOW 6.1 by Martin Bergvall at Tyréns. The groundwater flow model was stationary. Groundwater flow had to be determined with available information on geology and hydrogeology. A closer description of the groundwater flow model that forms the basis of the transport model constructed during this thesis work is given in the following sections.

4.4.1 Topography and soil type layers

Elevation data were given from previous investigations at the site (Sweco, 2008). The topography of Domsjö industrial site is relatively planar. Elevation, in RH70 height reference system, ranges from 7.6 m in the western part of the Western area to -0.63 m close to the shore line of River Moälven and Örnsköldsvik Bay. The groundwater surface at the site was assumed to follow topography.

More than 50 soil types were identified at the site (Sweco, 2008). Mixing of different soil types and fillings with wood residues complicated the procedure of estimating soil type layers with similar hydraulic conductivity. Slug-tests performed during groundwater sampling helped gain information of the hydraulic conductivity of the different soil types. However, to hurry the process of constructing a groundwater flow model, hydraulic conductivity at the entire site was set to an average value obtained from the slug-tests. Thus, spatial change in hydraulic conductivity was not taken into account when estimation of similar hydraulic conductivity in all layers was made.

4.4.2 Groundwater flow paths and model boundary

Flow paths of the groundwater at the site are partly depending on the regional flow from two larger watersheds (SMHI ID number: 702109-164447 and 702282-164700). The groundwater divide between the two watersheds, in Figure 8 called western and eastern watershed, is located in Domsjö industrial site, parallel to River Moälven (Figure 8) (SMHI, 2013).

Figure 8. The purple line crossing the landscape in Domsjö industrial site, parallel to River Moälven, shows the groundwater divide between the western and eastern watershed. The small polygon in red represents Domsjö industrial site. The blue area to the east of Domsjö industrial site is Örnsköldsvik Bay while the blue area to the west of Domskö industrial site is part of Själevad Bay.

Local flow paths of groundwater flow were determined with information available on measurements of hydraulic head. With previous measurements of hydraulic head at the site performed during the R&D project phase I in May 2009, isolines of groundwater surface was interpolated in FEFLOW to understand local flow paths (Figure 9). The assumed groundwater divide was approximated based on information of groundwater divide between the two larger watersheds and interpolated isolines in FEFLOW. Groundwater outflow from Domsjö industrial site was to River Moälven and Örnsköldsvik Bay.

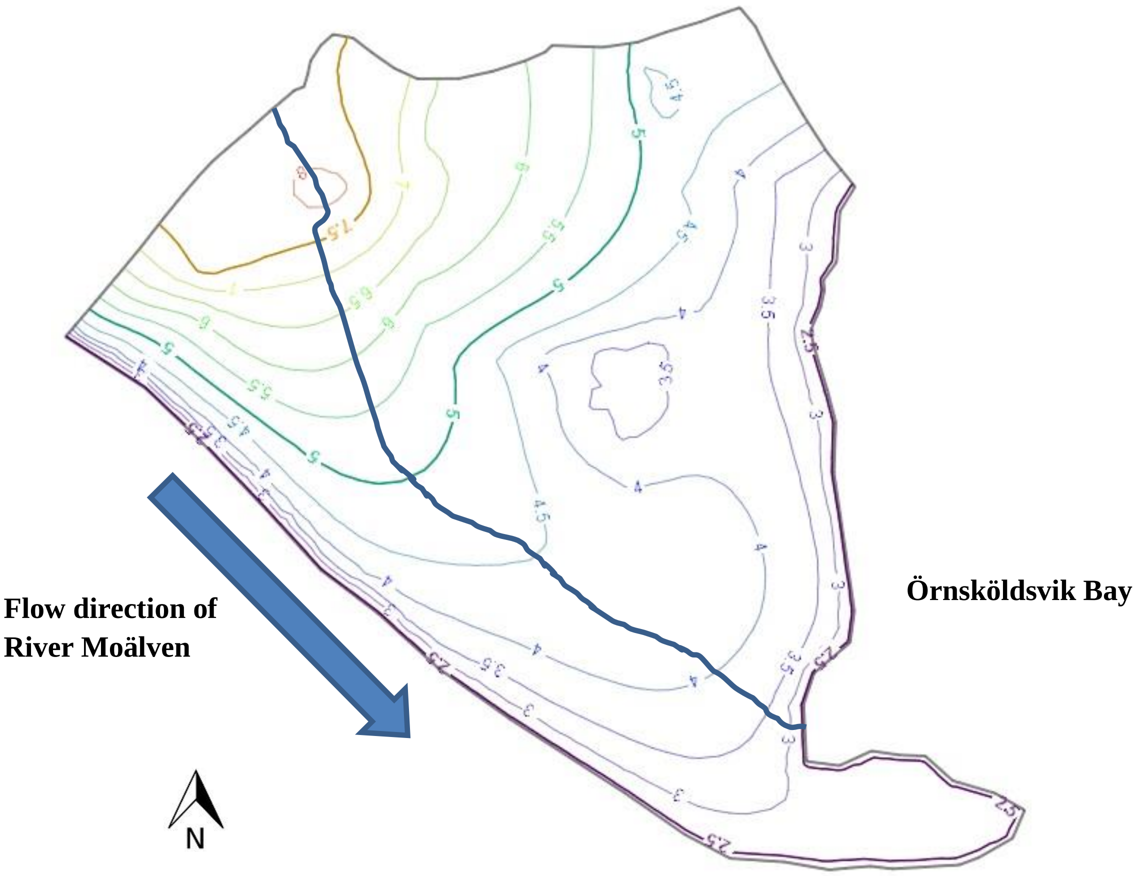


Figure 9. Interpolated isolines with an equidistance of 0.5 m showing the height of the groundwater table at Domsjö industrial site. The bold blue line represents the approximate location of the groundwater divide.

The outer boundary of the model was limited according to Figure 9. To the north and northeast, model boundary was parallel to the groundwater flow direction. Farther to the east along the shore line of Örnsköldsvik Bay, and along the shore line of River Moälven, model boundary was parallel to the interpolated isolines. Aquifer bottom boundary was determined by the distance to impermeable rock and almost impermeable clay.

Since Domsjö industrial site is located adjacent to Örnsköldsvik Bay, groundwater conditions are likely to be affected by sea level fluctuations. The constructed groundwater model was, however, in an initial stage assumed stationary. The hydraulic head close to the shore line of River Moälven and Örnsköldsvik Bay was therefore considered to not change over time.

Information about the location of storm water ditches at the site was given from maps constructed during the R&D project phase I. The depths of the storm water ditches were assumed to be 0.8 m.

4.4.3 Mesh design

The supermesh designed in FEFLOW consisted of one polygon representing the outer boundary of the model. The finite element mesh was designed in three dimensions as triangle prisms with six nodes per element. In total the mesh consisted of 9900 mesh elements and 6996 nodes. Mesh width was 894 m and mesh height was 804 m. The element length was no more than 20 m, i.e. less than two times the longitudinal dispersivity, which is suitable for stable calculations of contaminant transport.

The number of layers was set to three even though all layers were assigned similar properties. This was done because the work of developing a groundwater flow and transport model for Domsjö industrial site will continue even after this thesis work is completed. In FEFLOW the slice number is automatically set to number of layers + 1. The number of slices was therefore set to four.

4.4.4 Groundwater flow model boundary conditions and parameter values

The interpolated isolines at the northern part of Domsjö industrial site showed to be perpendicular to the model outer boundary. Therefore, no groundwater flow takes place across the model outer boundary. However, to account for regional groundwater flow from the two larger watersheds, one part of the northern border was set to have a constant inflow of groundwater (Figure 10). As described earlier, the groundwater flow model was stationary, why the hydraulic head of the entire shore line was assumed not to change. Transfer (Cauchy) boundary conditions were assigned to the storm water ditches as shown in Figure 10.

Based on the conceptual interpretation of groundwater flow patterns at the site, four types of boundary conditions were set in the groundwater flow model, illustrated in Figure 10 showing the topmost layer:

1. No flow at parts of the northern border was set in all four slices (grey lines).
2. Specific discharge of 0.0023 m/d from the two larger watersheds contributing to regional groundwater flow at the northern border was set in all four slices (pink crosses).
3. Specific head of 2.4 m in local height reference system close to the shore line of River Moälven and Örnsköldsvik Bay was set in all four slices (purple circles).
4. Fluid-transfer boundary condition at storm water ditches was set in the topmost and the second topmost slice of the model (green crossed circles). The outflow transfer rates of the ditches were set to 9 d^{-1} by assuming a 0.1 m thick clogging layer with a hydraulic conductivity of 1·10-5 m/s (five times lower than the K-value of the model). The inflow transfer rate (flow from the ditches to groundwater) was assumed to be relatively low and was set to 0.01 d^{-1}.

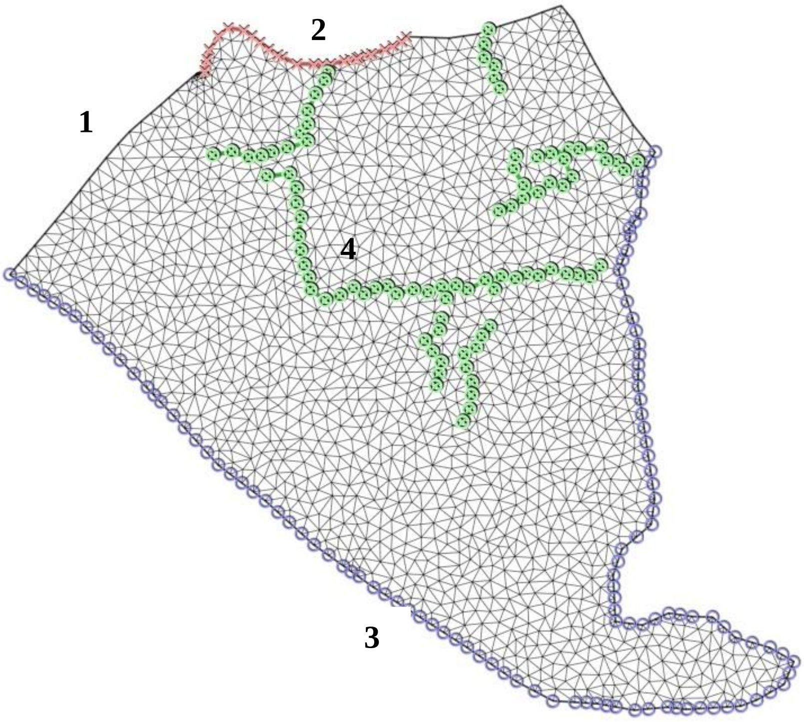


Figure 10. Boundary conditions of groundwater flow model at Domsjö industrial site: No-flow boundary condition specified by grey lines (1), Fluid-flux boundary condition pink crosses (2), Hydraulic-head boundary condition purple circles (3) and Fluid-transfer boundary condition (ditches) green crossed circles (4).

In Table 3 parameter values used as input to the groundwater flow model are declared.

Table 3. Values of parameters affecting groundwater flow.

Parameter	Value
Longitudinal hydraulic conductivity K_x [m/d]	5
Horizontal hydraulic conductivity K_y [m/d]	5
Vertical hydraulic conductivity K_z [m/d]	2
Inflow on top slice (i.e. groundwater recharge) [m/d]	$5.14 \cdot 10^{-4}$ [a]
Drain-/fillable porosity ε [-]	0.2
Specific storage [m^{-1}]	$1.0 \cdot 10^{-4}$
In transfer-rate (fluid) [d^{-1}]	0.01
Out transfer-rate (fluid) [d^{-1}]	9
Porosity [-]	0.3

[a] See appendix A.

4.4.5 Calibration of the groundwater flow model

The groundwater model was calibrated by comparing modeled hydraulic head to measured hydraulic head in 40 groundwater observation wells at the site. Figure 11 shows modeled hydraulic head after simulation time of six years. Simulation time was chosen to six years because calibration data for the transport model, described further in section 4.5 CONCEPTUAL TRANSPORT MODEL, only was available after six years. Seasonal variations were not taken into account. The figure shows the locations of all boundary conditions, together with the location of the 40 groundwater observation wells, marked with green dots and observation flags.

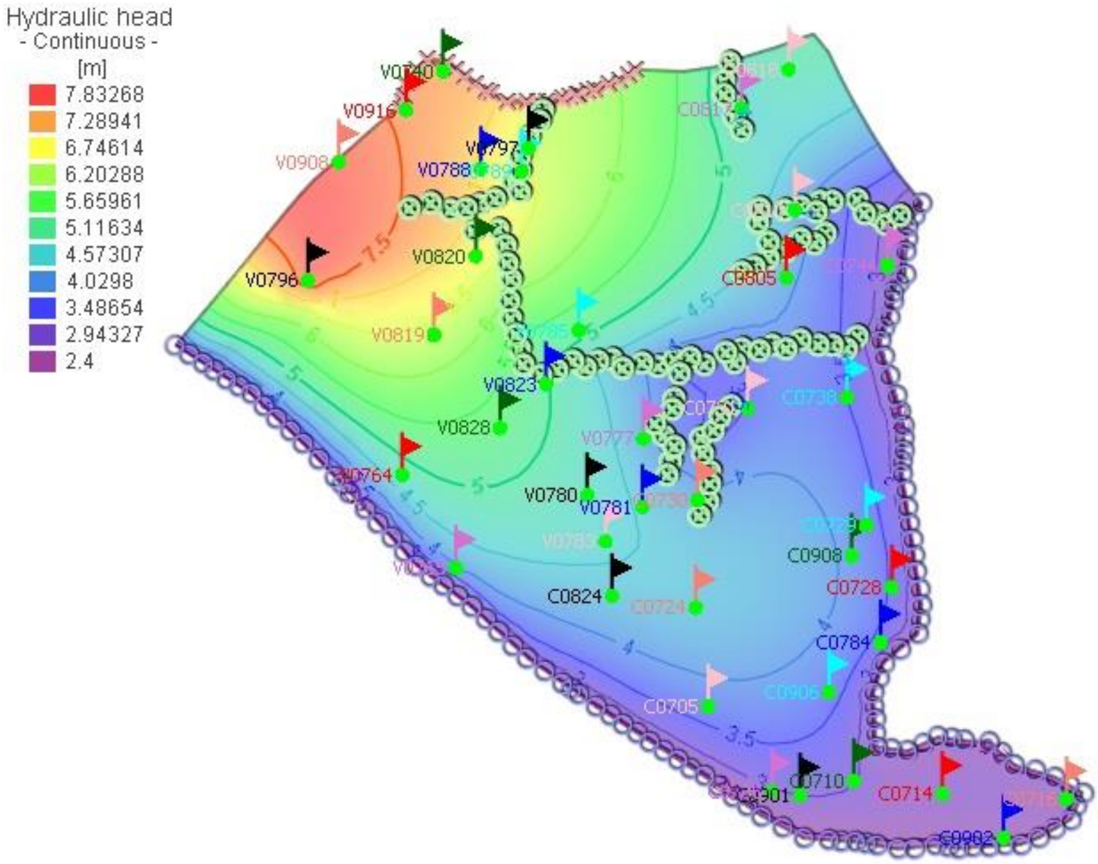


Figure 11. Simulated hydraulic head at the site after six years together with isolines with an equidistance of 0.5 m. The 40 groundwater observation wells are marked with green dots and observation flags.

To evaluate the model´s ability to represent reality groundwater flow was simulated for six years. Results from groundwater flow simulation at the site showed that modeled hydraulic head correspond to measured hydraulic head in all 40 observation points (Figure 12). The slope of the fitted regression line with equation has a value close to 1 and R^2 value of 0.999. One probable reason why modeled values correspond well to measured values is that several of the groundwater observation wells are located closely to the model boundary conditions.

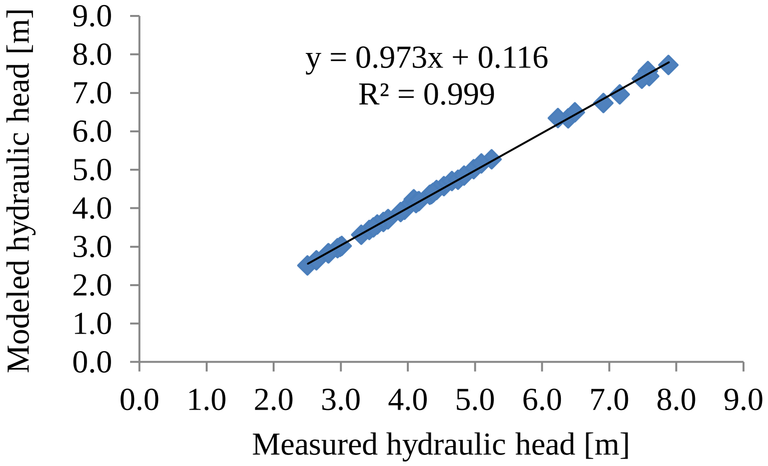


Figure 12. Modeled hydraulic head after six years plotted versus measured hydraulic head shows that the groundwater flow model well predicts groundwater flow at the site. A fitted regression line with slope 0.973 has been added to the plot.

4.5 CONCEPTUAL TRANSPORT MODEL

The transport model was based on the previously described groundwater flow model constructed in FEFLOW 6.1. Simulation of contaminant concentration was therefore also made in FEFFLOW 6.1. The contaminants phenanthrene and DEHP were assumed to be partitioned to DOC with partitioning coefficient K_{DOC} and transported with DOC in groundwater as an advective-dispersive process. The contaminant sources were unknown when performing this thesis work. Assumption of contaminant sources had to be made to be able to construct a transport model for the contaminants, described further in section 4.5.2 Contaminant sources. Since the contaminants are assumed to follow groundwater flow they will be transported towards the recipients River Moälven and Örnsköldsvik Bay.

For calculating contaminant concentration in groundwater, the mobility equation recommended by Swedish EPA (2009b) was used. Besides information of contaminant concentration in the soil (C_s) and K_{DOC} values, also DOC content, K_d values, θ_w and θ_a, H and ρ_b for each contaminant at several observation points was needed. A closer description of the different simulated scenarios, contaminant sources and DOC distribution is given in the sections below.

4.5.1 Scenario description

To investigate mobility of the contaminants based on different K_{DOC} values, five scenarios were set up. For phenathrene, the tabulated K_{DOC} values obtained from Burkhard (2000) were to be tested based on the lowest (K_{DOC} min), the highest (K_{DOC} max) and median (K_{DOC} median) value to evaluate which one were best fitted for phenanthrene at Domsjö industrial site. For DEHP, equation 12 and 10 were used to calculate K_{DOC} from K_{OC} and K_{OW} respectively. The five scenarios are described in Table 4.

Table 4. The five different scenarios of simulated contaminant concentration together with the different K_{DOC} values.

Scenario	Description	K_{DOC} [L/kg]
1	Transport of phenanthrene with K_{DOC} min	8128.3[a]
2	Transport of phenanthrene with K_{DOC} max	3162277.7[a]
3	Transport of phenanthrene with K_{DOC} median	32359.4[a]
4	Transport of DEHP with K_{DOC} calculated with K_{OC}	24000
5	Transport of DEHP with K_{DOC} calculated with K_{OW}	$1.1 \cdot 10^6$

[a] Burkhard, 2000.

As described earlier, the mobility equation needs information about contaminant concentration in the soil. Since the field study was performed during winter, newer soil samples needed to measure soil contaminant concentration could not be made. Initial values of contaminant concentration in the soil had to be taken from measurements performed in 2007. Since the thesis work was performed in 2013 simulation time was set to six years for all scenarios to be able to compare modeled contaminant concentration in groundwater to measured contaminant concentration.

4.5.2 Contaminant sources

When modeling contaminant transport in groundwater it is essential to have information about the sources of contamination to understand how the contaminants move through the soil at the actual site. The only information available about contamination source for both phenanthrene and DEHP was that they probably result from production, storage and leakage of various chemical substances and metabolites (Sweco, 2008). The location of this production, storage and leakage was unfortunately unknown.

To create a possible source of contamination as input to the transport model constructed in this thesis work, a few assumptions had to be made. Even though information about contamination source was unknown, concentration of contaminants in the soil measured in 2007 gave a clue about the location of contamination sources. For phenanthrene, C_s was available in 324 sampling points. For DEHP, C_s was available in 40 sampling points. The studied organic contaminants are both persistent and are therefore assumed to retain in the soil for longer periods of time. Due to the short simulation time of six years in this context, contamination situation from 2007 to 2013 was assumed to not change in a large extent. To be able to compare modeled concentrations with measured from 2013, simulation time was set to six years (from 2007 to 2013). The conceptual interpretation was that contaminants in the soil leak to groundwater due to precipitation.

Initial values of mobile contaminant concentration in the groundwater (C_{w_mob}) were calculated with the mobility equation based on contaminant concentration in the soil from measurements performed in 2007. Unfortunately, the locations of measured values of C_s performed in 2007 were not synchronized with measured values of DOC performed in 2013. Distribution of C_s and DOC for both of the contaminants at the site was therefore interpolated in ArcMap 10.1 with spatial analyst tool using Natural Neighbor method to create a density map of the concentration of each contaminant and DOC in the soil. Thus, C_s and DOC were synchronized in all sampling points and C_{w_mob} was calculated.

The distribution of C_{w_mob} was interpolated in FEFLOW, described in Figure 13 and 14 for phenanthrene and DEHP respectively. Highest concentration of phenanthrene in the soil samples (and therefore also C_{w_mob}) was to the southwest of Domsjö industrial site (in the Western area), close to the shore line of River Moälven. Highest concentration of DEHP seemed to be in the southern region, close to River Moälven but also close to Örnsköldsvik Bay.

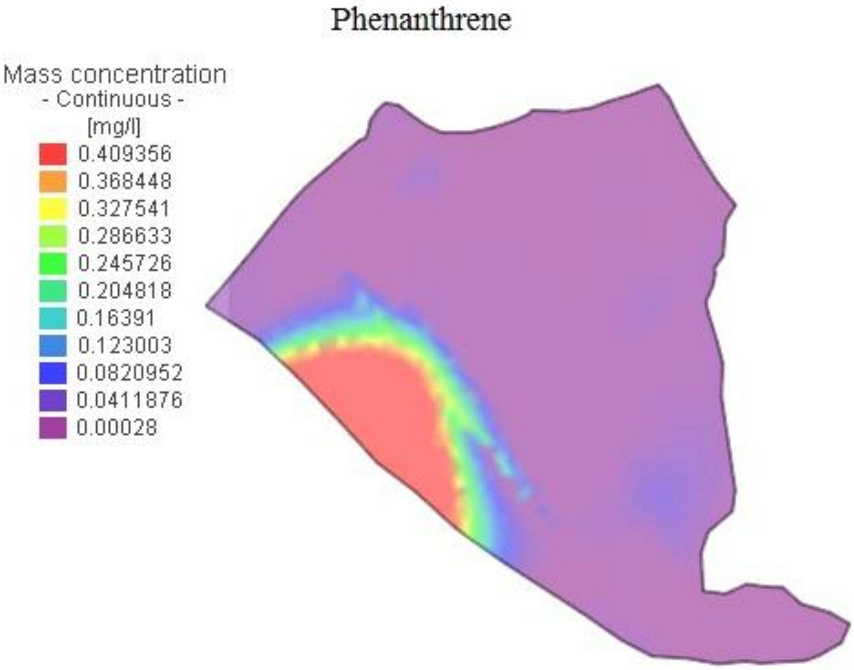


Figure 13. Initial values of C_{w_mob} for phenanthrene calculated with the mobility equation. The phenanthrene distribution seemed to be concentrated in the southwestern part of Domsjö industrial site, close to the shore line of River Moälven.

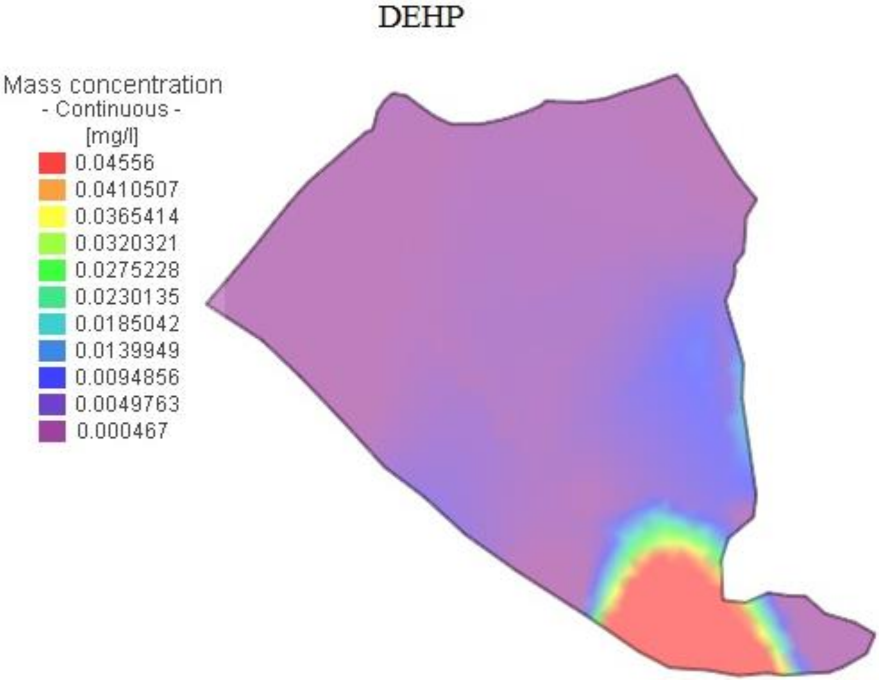


Figure 14. Initial values of C_{w_mob} for DEHP calculated with the mobility equation. The DEHP distribution seemed to be concentrated in the southern part of Domsjö industrial site, close to River Moälven but also close to Örnsköldsvik Bay.

Precipitation at the site was assumed to affect the groundwater flow by changing the hydraulic gradient, causing contaminants bound to DOC to transport with the groundwater towards River Moälven and Örnsköldsvik Bay. Contribution of regional groundwater flow from the two larger watersheds was also assumed to cause contaminants partitioned to SOM to leak to groundwater at the northern part of Domsjö industrial site. Thus, contaminant sources were assumed to be constantly infused to groundwater with precipitation and by inflow of regional groundwater flow from the two larger watersheds.

4.5.3 DOC degradation and retardation

Movement of DOC in the soil may cause DOC to be retarded by adsorbing to mineral surfaces, or degraded by microbes (Inamdar et al. 2012). However, to keep the model as simple as possible, impact of these processes were neglected during construction of the conceptual model.

4.6 NUMERICAL MODEL

4.6.1 Transport model boundary conditions and constraints

One of the contaminant sources to Domsjö industrial site was considered to result from inflow of regional groundwater flow at the northern border. In all three layers C_{w_mob} for both contaminants close to the border was calculated from C_s and set as mass-concentration boundary condition. During the very first simulation (scenario 4 – Simulation of DEHP in groundwater with K_{DOC} from K_{OC}), model calculations caused an inflow of negative contaminant concentration. A constraint of 0 g/d was therefore set.

The other contaminant source was leakage of contaminants in the soil to groundwater. Inflow of the contaminants from the topmost layer to the second layer and eventually third layer was calculated with equation 16. To account for possible miscalculations within the model a constraint of 0 g/d was set.

$$Inflow\ to\ topmost\ layer = C_{w\_mob} \cdot P \qquad (16)$$

Where C_{w_mob} is concentration of mobile contaminant [mg/L] and P is precipitation [m/d].

The following boundary conditions for the transport model were set based on the conceptual interpretation of contaminant transport in the soil and groundwater at the site, illustrated in Figure 15:

1. Mass-concentration boundary condition in all four slices at the northern border (purple circles with underlines) based on contaminant concentrations close to the border. A constraint was set to 0 g/d to eliminate model errors of calculating negative concentration of contaminant inflow. By that means that groundwater can still flow across the boundary but contaminant concentration is automatically set to > 0 g/d.
2. Mass-concentration boundary condition in all four slices at the shore line (purple circles with underlines) was set to 0 mg/L. A positive flux of solutes from the model domain over the boundary was possible, but a constraint was set to 0 g/day restricting inflow of contaminants from River Moälven and Örnsköldsvik Bay.
3. Mass-flux boundary condition in the topmost slice (pink crosses) of calculated concentration C_{w_mob} [mg/L] based on K_{DOC} values and mean groundwater recharge (or precipitation) as in equation 16. No constraint was necessary.
4. Mass-concentration boundary condition in the top most and the second topmost slices at storm water ditches (purple circles with underlines) was set to 0 mg/L based on the contamination source assumption of contaminant inflow only at the northern border and with groundwater recharge. Also here a constraint was set to 0 g/day.

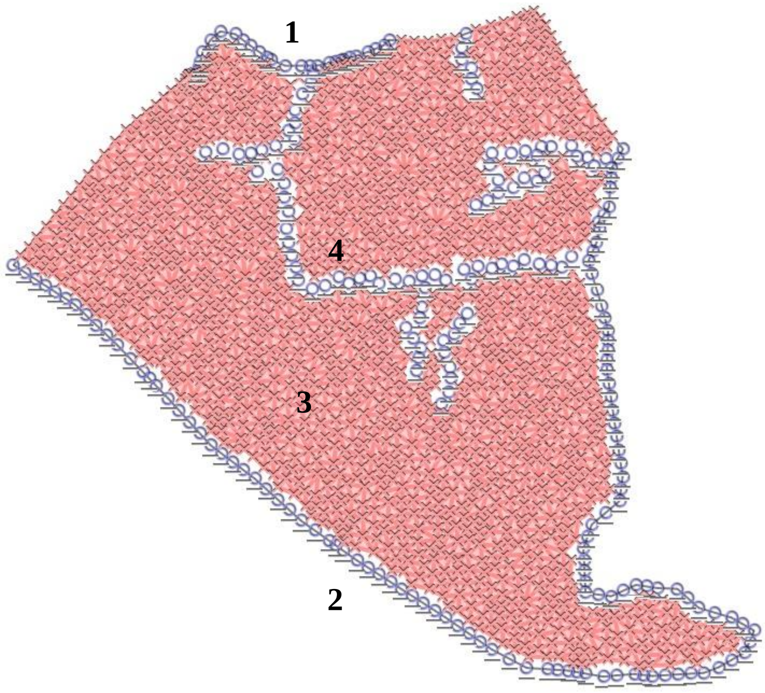


Figure 15. Transport model boundary conditions and constraints with purple circles representing mass-concentration boundary condition with constraint of 0 g/d (1, 2 & 4) and pink crosses representing mass-flux boundary condition (3).

Values of the boundary conditions for all scenarios are shown in Table 5.

Table 5. Values of the transport model boundary conditions for every scenario.

	Mass-concentration boundary condition (1) [mg/L]	**Mass-concentration boundary condition (2) [g/d]**	**Mass-flux boundary condition (3)**	**Mass-concentration boundary condition (4) [g/d]**
Scenario 1	0.00021	0	From shapefile	0
Scenario 2	0.015	0	From shapefile	0
Scenario 3	0.0003	0	From shapefile	0
Scenario 4	0.0004	0	From shapefile	0
Scenario 5	0.008	0	From shapefile	0

The transport model for all five scenarios was calibrated to fit the first simulation (scenario 4). Further calibration of each scenario would generate different conditions for contaminant transport and since only K_{DOC} values were to be evaluated in this thesis work all five scenarios were calibrated after identical conditions.

4.6.2 Transport model parameters

The mobility equation requires knowledge about both site specific and contaminant specific constants and variables. Most of the input to the equation had to be estimated since site specific values were not available. K_d values for each contaminant should, if possible, be generated from tabulated values (Swedish EPA, 2009b). If no such values are available, K_d may be calculated with equation 17.

$$K_d = K_{OC} \cdot f_{OC} \qquad (17)$$

Where K_{OC} is the distribution coefficient between water and organic carbon [L/kg] and f_{oc} is the mass fraction of organic carbon [-].

K_d values had to be calculated for both phenanthrene and DEHP. f_{oc} of the soil at the site was estimated to an average value of 0.0098 (Sweco, 2008).

Soil water content θ_w and soil air content θ_a was set to estimated values specific for fine sand. Values of Henry's constant H for both phenanthrene and DEHP were taken from the literature and the bulk density ρ_b was estimated to a default value based on porosity and sand grain density.

Adsorption coefficient K_a of each contaminant was calculated with equation 18.

$$K_a = K_d \cdot \rho_s = K_d \cdot \frac{\rho_b}{1-\varepsilon} \qquad (18)$$

Where K_d is the soil/water distribution coefficient [L/kg], ρ_s is solid density [kg/L], ρ_b is the bulk density [kg/L] and ε is the drain-/fillable porosity [-].

All of the input parameter values for simulation of fluid flow and mass transport are described in Table 6.

Table 6. Input parameters of mass transport to FEFLOW 6.1.

Parameter	**Phenanthrene**	**DEHP**
Adsorption coefficient K_a [-]	477	2083
Molecular diffusion [m^2/s]	$1 \cdot 10^{-9}$	$1 \cdot 10^{-9}$
Longitudinal dispersivity [m]	13	13
Transverse dispersivity [m]	1.3	1.3
Decay-rate constant [s^{-1}]	0	0
Soil/water distribution coefficient K_d [l/kg]	224.5	980
Soil water content θ_w [dm^3 water/dm^3 soil]	0.1	0.1
Soil air content θ_a [dm^3 air/dm^3 soil]	0.35	0.35
Henry's constant H [$\cdot 10^{-5}$ atm·m^3/mol]	3.35[a]	1.1[b]
Bulk density ρ_b [kg/dm^3]	1.7	1.7

[a] Odabasi et al., 2006.

[b] Howard, 1989.

5 RESULTS

5.1 GROUNDWATER SAMPLING

The groundwater at Domsjö industrial site was characterized by low phenanthrene and DEHP content together with high DOC content. Results from laboratory analysis show that all of the samples had contaminant concentration below the guideline value SRC_{eco} = 30 µg/L for phenanthrene and SRC_{eco} = 5.0 µg/L for DEHP. Out of the ten analyzed groundwater samples of phenanthrene three had concentration below detection limit 0.01 µg/L while five of the groundwater samples had concentration below detection limit 1.3 µg/L for DEHP. Highest reported concentration of phenanthrene and DEHP occurred at sampling points C0728 and C0738 close to the shore line of Örnsköldsvik Bay, to the west of Domsjö industrial site. Also DOC was present in highest concentration in these two points. Table 7 shows the concentration of each substance in all sampling points where cells marked with red and orange color shows highest and second highest reported concentration. For a plot of contaminant concentration versus DOC concentration in the sampling points, see appendix B.

Table 7. Concentration of DOC and contaminants in the sampling points. Red cells represents the highest concentration of each analyzed substance. Orange cells represents the second highest concentration of each analyzed substance.

Point	DOC [mg/L]	Phenanthrene [µg/L]	DEHP [µg/L]
C0705	171	-	-
C0708	233	-	-
C0710	33.4	-	-
C0724	5.98	0.01	<1.3
C0728	814	0.24	3.7
C0738	1070	1.1	3.1
C0744	147	0.09	1.4
C0805	81.5	0.02	<1.3
C0810	58.4	<0.01	1.5
C0817	37.9	0.02	<1.3
V0777	127	0.02	<1.3
V0781	310	-	-
V0785	86.3	-	-
V0796	12.9	-	-
V0819	8.31	<0.01	<1.3
V0820	55	-	-
V0823	177	<0.01	3
V0916	42.7	-	-
V0925	17.6	-	-

5.2 MODEL RESULTS

5.2.1 Scenario 1 – Phenanthrene in groundwater with K_{DOC} min value

Simulation of phenathrene transport after six years with minimum K_{DOC} value = 8128.3 L/kg shows phenanthrene to still be concentrated in the areas closest to River Moälven (Figure 16). Simulated phenanthrene concentration has decreased compared to initial values from 2007. Compared to measured values from 2013, the simulation shows an average under-estimation of phenanthrene concentration in the seven observation points with detectable measured phenanthrene concentration (appendix C). Simulation was performed with 118 time step iterations.

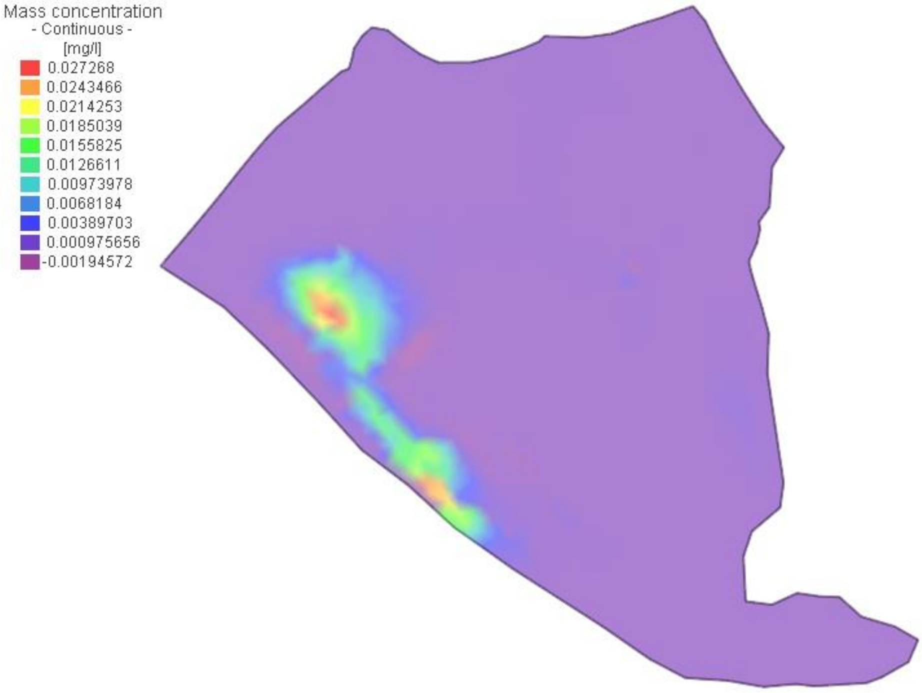


Figure 16. Distribution of phenathrene in the topmost slice with simulation scenario 1 at Domsjö industrial site after six years of simulation.

5.2.2 Scenario 2 – Phenanthrene in groundwater with K_{DOC} max value

Simulation of phenathrene transport after six years with maximum K_{DOC} value = 3162277.7 L/kg shows phenanthrene to still be concentrated in the areas closest to River Moälven, as for scenario 1 (Figure 17). Simulated phenanthrene concentration has increased compared to initial values from 2007. Compared to measured values from 2013, the simulation shows an average over-estimation of phenanthrene concentration in the seven observation points with detectable measured phenanthrene concentration (appendix C). Simulation was performed with 129 time step iterations.

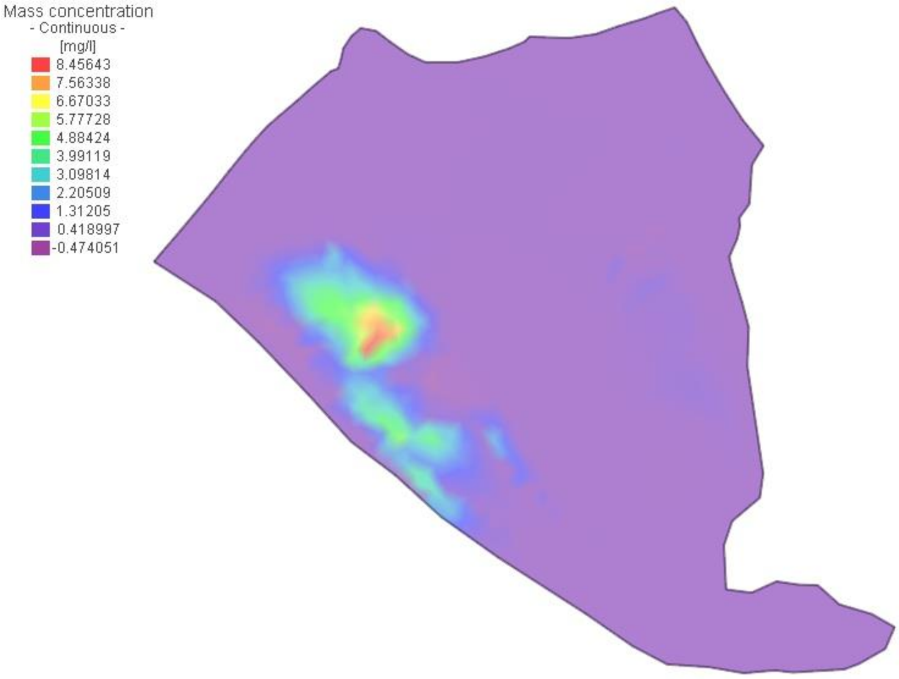


Figure 17. Distribution of phenathrene in the topmost slice with simulation scenario 2 at Domsjö industrial site after six years of simulation.

5.2.3 Scenario 3 – Phenanthrene in groundwater with K_{DOC} median value

Simulation of phenathrene transport after six years with median K_{DOC} value = 32359.4 L/kg shows phenanthrene to still be concentrated in the areas closest to River Moälven, as for scenario 1 and 2 (Figure 18). Simulated phenanthrene concentration has decreased compared to initial values from 2007. Compared to measured values from 2013, the simulation shows an average over-estimation of phenanthrene concentration in the seven observation points with detectable measured phenanthrene concentration (appendix C). Simulation was performed with 121 time step iterations.

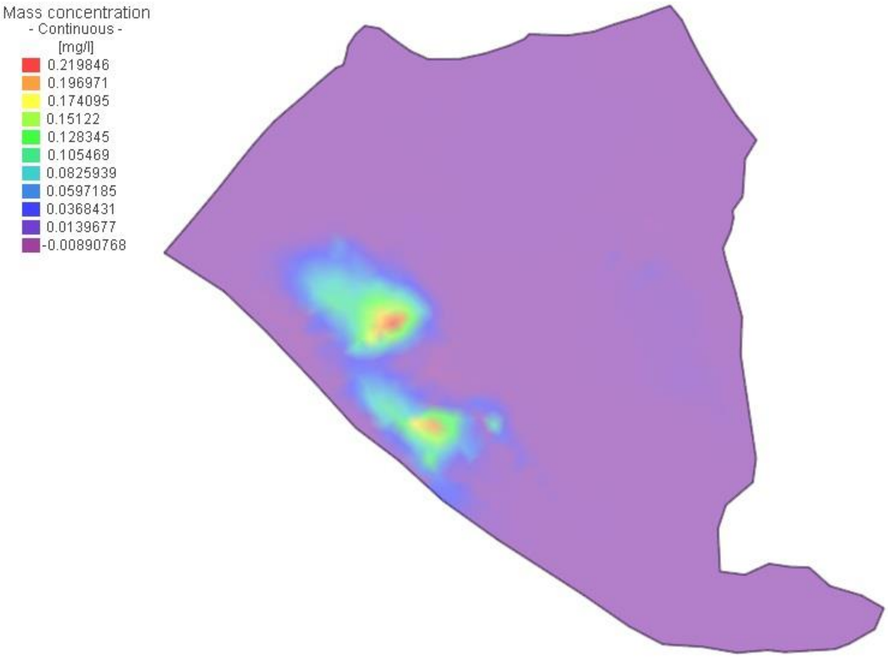


Figure 18. Distribution of phenathrene in the topmost slice with simulation scenario 3 at Domsjö industrial site after six years of simulation.

5.2.4 Scenario 4 – DEHP in groundwater with K_{DOC} from K_{OC}

Simulation of DEHP transport after six years with K_{DOC} = 2400 L/kg calculated with K_{OC} shows DEHP to be concentrated in the areas closest to Örnsköldsvik Bay (subareas C4 – C6) and further south to River Moälven (subarea C1) (Figure 19). Simulated DEHP concentration has decreased compared to initial values from 2007. Compared to measured values from 2013, the simulation shows an under-estimation of DEHP concentration in the five observation points with detectable measured DEHP concentration (appendix C). Simulation was performed with 51 time step iterations.

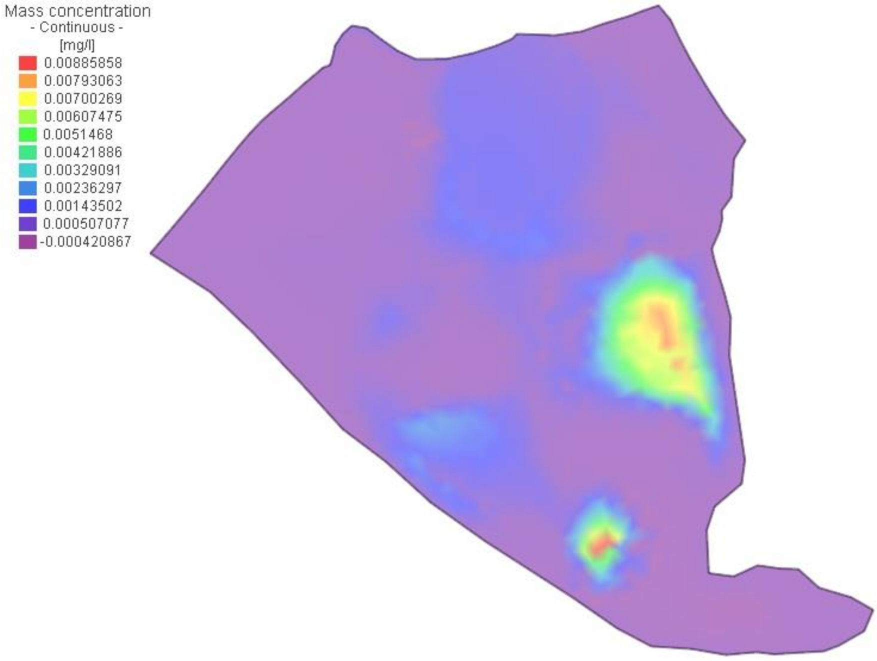


Figure 19. Distribution of DEHP in the topmost slice with simulation scenario 3 at Domsjö industrial site after six years of simulation.

5.2.5 Scenario 5 – DEHP in groundwater with K_{DOC} from K_{OW}

Simulation of DEHP transport after six years with K_{DOC} value = 1096705.4 L/kg calculated with K_{OW} shows DEHP to be concentrated in the areas closest to Örnsköldsvik Bay (subareas C4 – C6) (Figure 20). Simulated DEHP concentration has increased compared to initial values from 2007. Compared to measured values from 2013, the simulation shows an over-estimation of DEHP concentration in the five observation points with detectable measured DEHP concentration (appendix C). Simulation was performed with 48 time step iterations.

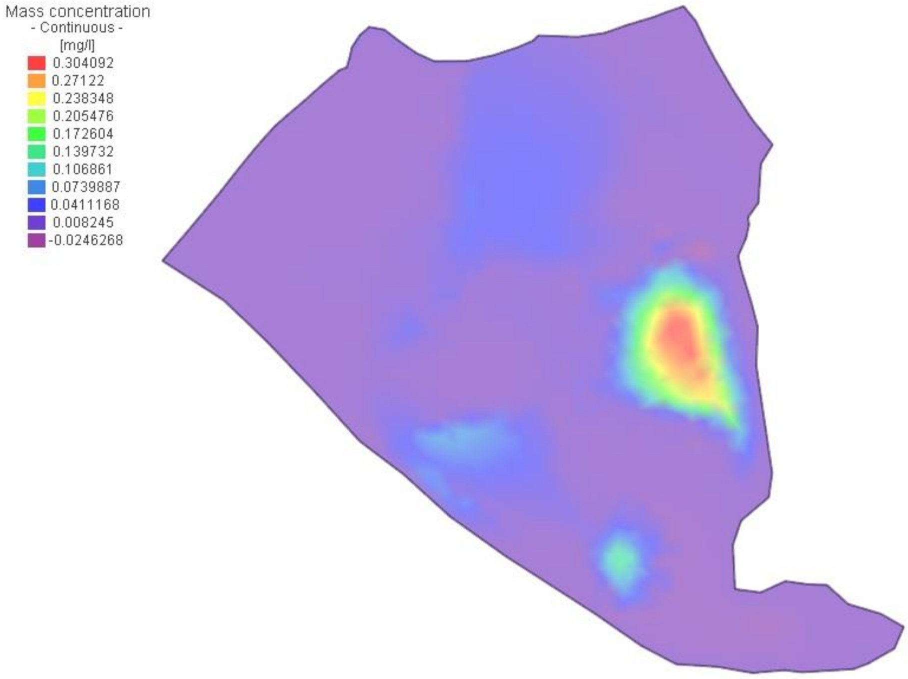


Figure 20. Distribution of DEHP in the topmost slice with simulation scenario 3 at Domsjö industrial site after six years of simulation.

5.3 MODEL RESIDUALS

Comparison of the mean absolute error for all five scenarios showed scenario 1, 3 and 4 to have the lowest values of mean absolute error. Mean absolute error for scenario 1, 3 and 4 was 0.000102, 0.000164 and 0.00136 respectively (Figure 21). Best approximation of phenanthrene concentration in the groundwater was, according to the mean absolute error, achieved with scenario 1 – K_{DOC} minimum value. Best approximation of DEHP concentration in the groundwater was, according to the mean absolute error, achieved with scenario 4 – K_{DOC} calculated from K_{OC}. The mean absolute error for scenario 2 and 5 was 0.0125 and 0.0289 respectively.

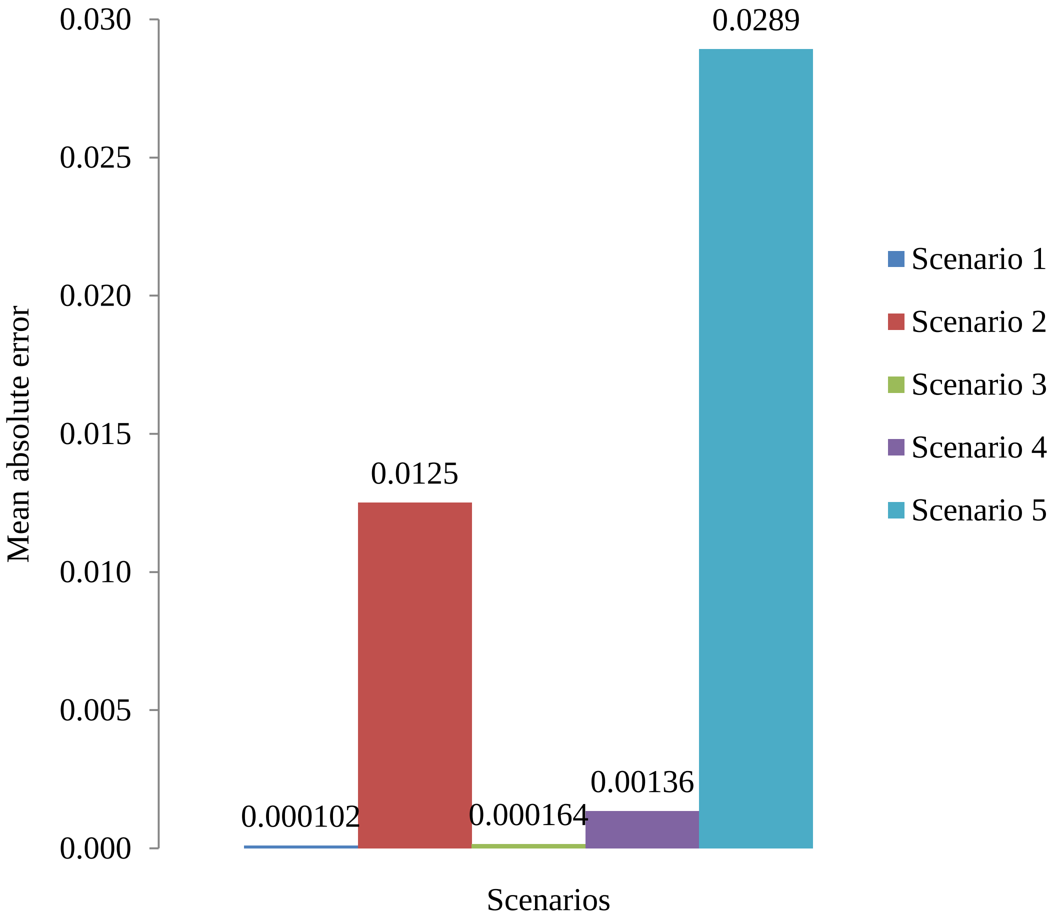


Figure 21. Calculated mean absolute error of the five transport model scenarios.

5.4 CORRELATION OF DOC AND PHENANTHRENE

The log-log linear relationship between phenanthrene and DOC is shown in Figure 22 where log phenanthrene is plotted to log DOC. A fitted regression line has been estimated in Microsoft Excel. The 3 samples with concentration below detection limit have been removed before performance of the correlation test that only was made with the 7 samples with concentration above detection limit for phenanthrene.

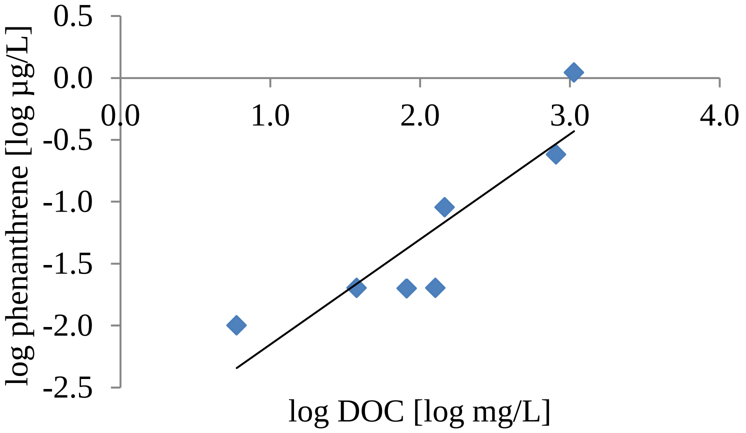


Figure 22. Measured log phenanthrene [log µg/L] plotted to measured log DOC [log mg/L] shows a log-log linear relationship between phenanthrene and DOC.

Correlation coefficient R was calculated to 0.89 and p-value was 0.007. Comparison of the p-value with predetermined $\alpha = 0.05$ shows that p-value $< \alpha$ and H_0 (there is no covariance) is rejected. There is a significant correlation between DOC and phenanthrene at 99% confidence level.

5.5 CORRELATION OF DOC AND DEHP

The log-log linear relationship between DEHP and DOC is shown in Figure 23 where log DEHP is plotted to log DOC. A fitted regression line has been estimated in Microsoft Excel. The 5 samples with concentration below detection limit have been removed before correlation analysis that only was performed on the 5 samples with concentration above the detection limit.

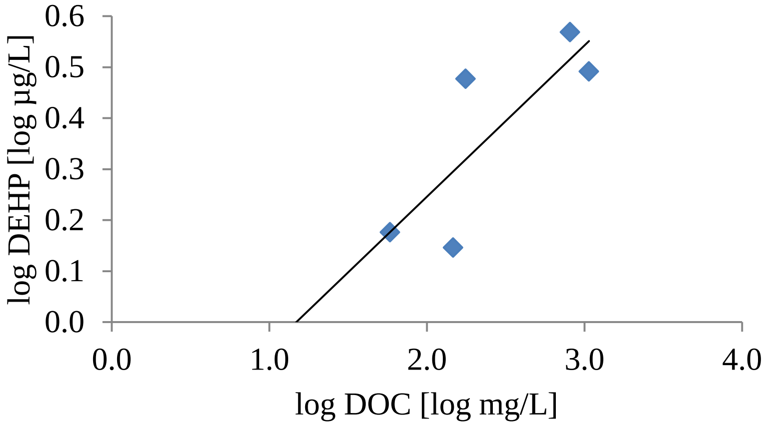


Figure 23. Measured log DEHP [log µg/L] plotted to measured log DOC [log mg/L] shows a log-log linear relationship between DEHP and DOC.

Calculated correlation coefficient R was 0.81 and p-value was 0.099. Since p-value > α = 0.05, H_0 is confirmed. There is not a significant correlation between DOC and DEHP at 95% confidence level. However, at 90% confidence level there is a significant correlation between DOC and DEHP since p-value < 0.1.

6 DISCUSSION

6.1 K_{DOC} VALUES AND CONTAMINANT CONCENTRATIONS

Of the investigated K_{DOC} values for phenanthrene the minimum and median value of K_{DOC} proved to best model phenanthrene concentration after six years compared to measured values. Calculations based on maximum K_{DOC} value clearly over-estimated modeled phenanthrene concentration. The best result of modeled C_{w_mob} for DEHP was obtained with K_{DOC} calculated from K_{OC} even though modeled concentrations were under-estimated. DEHP concentrations simulated with K_{DOC} from K_{OW} were over-estimated compared to measured concentrations. C_{w_mob} was calculated with the mobility equation (equation 13), that requires input such as C_s, K_{DOC} and DOC along with other site and contaminant specific parameters. Since DOC concentration used in the equation originates from measured values and all other parameters remain constant during all simulations, C_s and K_{DOC} are the two parameters most likely affecting under- and over-estimations. Of course the other parameters might also be sources of error, which is why the model predictability is difficult to evaluate.

Measured C_s from 2007 was not available in all sampling points where DOC was measured during this thesis work in 2013, why an interpolation in ArcMap 10.1 was performed with the Natural Neighbor method. This interpolation method assumes C_s and DOC to be evenly distributed at the site which in reality might not be the case. In reality concentrations of each contaminant might result from point sources but this was not taken into account during this thesis work. However due to the need of C_s and DOC in all sampling points, to be able to evaluate the mobility equation, an interpolation had to be made. Sources of error resulting from this interpolation method have to be taken into account when evaluating model prediction ability. The optimal situation would, of course, include site specific constants and more measurements of contaminant concentration in soil and groundwater.

Tabulated values of DEHP log K_{OW} were available in a range of 4.8 – 9.6. In this thesis work a value of 7.1 was chosen for log K_{OW} due to recommendations from Howard et al. (1985). Since DEHP easily forms colloids in water phase a high value of log K_{OW} is expected. However, the high K_{OW} produces a high K_{DOC} which in turn seems to over-estimate DEHP concentration in groundwater. In the Swedish EPA report (2009b) K_{DOC} is recommended to be calculated with K_{OC} if no tabulated values of K_{DOC} for the contaminant are available. The relationship of K_{OW} and K_{DOC} described by Burkhard (2000) might not be suitable for DEHP.

Based on the results from the thesis work, it is not possible to determine whether tabulated or calculated values of K_{DOC} better estimate contaminant concentration. Comparison of tabulated values for phenanthrene and calculated values for DEHP would not give a valid conclusion. With hindsight, it would have been best to have access to tabulated and calculated K_{DOC} values for one single contaminant for comparison of tabulated versus calculated values.

Laboratory analysis of PAHs and phthalates in groundwater showed surprisingly low concentration of phenanthrene and DEHP. According to Sweco (2008) both contaminants had concentrations exceeding Swedish EPA's guideline values especially in the subareas closest to the shore line in the Cistern area. In this thesis work the contaminants were present in highest concentration also in this area (points C0728 and C0738). This implies that contaminants may already have leached to Örnsköldsvik Bay.

In a later stage of the thesis work it was found that results from the screening analysis performed in 2007 were not included in the input file for C_s. The screening analysis showed higher C_s than reported in the original file. These results might show a more representative picture of the contamination situation in the soil. Nonetheless, with higher C_s, calculated C_{w_mob} would also increase giving an even higher initial value of C_{w_mob} than showed in this thesis work. Compared to the measured C_{w_mob} it would also increase model residuals. As previously mentioned, the optimal situation would be to have analytical results of soil samples in all points where the groundwater samples were analyzed.

6.2 CONCEPTUAL AND NUMERICAL MODEL

Simulation of groundwater flow after six years showed that modeled hydraulic head was similar to measured hydraulic head even though all of the layers were assumed to have same material properties as porosity and hydraulic conductivity. In reality, this is probably not the case. Due to the many different soil types and mixing with industrial residues as wood residues at Domsjö industrial site the process of characterizing soil type layers for this thesis was delayed and estimation of similair hydraulic conductivity in all layers had to be done. Nonetheless, applied hydraulic conductivity in the model results from slug tests performed at the site which indicates a trustworthy assumption of average hydraulic conductivity. Due to the well-fitted groundwater flow model, over- and under-estimations of contaminant concentrations are assumed to mostly depend on transport model calculations and not on the groundwater flow simulation. As described earlier, one probable reason for the well-fitted groundwater flow model might be that many of the groundwater observation wells are located close to the model boundaries. A further investigation of the constructed groundwater flow model is necessary to evaluate the predictability of the transport model.

Since the aim of the thesis work was to evaluate importance of DOC for organic contaminants the assumption of no degradation and retardation of DOC and contaminants was made to simplify the modeling process. According to Inamdar et al. (2012) faster flow paths such as surface runoff and groundwater flow in larger macro pores may reduce residence time and the microbial consumption of DOC may be neglected in such cases. As for retardation of DOC, a faster flow path contributes to less retardation because of shorter contact time between DOC and soil minerals. Neglecting of degradation and retardation of DOC and contaminants may be the reason why modeled and measured results differ.

All five transport model scenarios were calibrated to fit the first simulation (scenario 4). Further calibration of each scenario would, as described earlier, generate different conditions for contaminant transport and since only K_{DOC} values were to be evaluated during this thesis work all five scenarios were calibrated after identical conditions. It might be that all scenarios do not fit boundary conditions set for scenario 4 but by changing parameters and boundary conditions to fit each scenario, it means that also parameters other than K_{DOC} are investigated.

Prediction ability of the transport model is difficult to estimate due to lack of data needed for validation of the model. Three of the five studied scenarios over-estimated modeled contaminant concentration after six years while two of them under-estimated contaminant concentration. Complementary measurements, in additional groundwater observation wells, would provide validation data needed for the transport model.

6.3 CORRELATION OF DOC WITH CONTAMINANTS

One way of evaluating importance of DOC for transport of organic contaminants was to simply estimate correlation of DOC and contaminants in a few observation points. The result showed a significant correlation between DOC and phenanthrene at 95% confidence level. In fact, phenanthrene showed significant correlation with DOC even at 99% confidence (calculated p-value of $0.007 < \alpha = 0.01$). However, the statistical analysis performed during this thesis work was not multivariate. The correlation test executed in this thesis work does not take other variables possibly affecting both of the others into account. Theoretically, there might be a third variable affecting both contaminant concentration and amount of DOC. However, that was not the purpose of the thesis work to investigate.

The relationship of DEHP and DOC did not show significant correlation at the 95% confidence level even though the DEHP concentration was high in same sampling points as DOC concentration was high. Due to small amount of samples (five that were above detection limit) DEHP needed a higher R value than phenanthrene to show significance. Even if DOC did not show significant correlation with DEHP at 95% confidence level, the calculated p-value of DEHP was 0.099 resulting in a significant correlation at 90% confidence level. Additional measurements of DEHP and DOC may show a significant correlation also at 95% confidence level.

6.4 FURTHER STUDIES

Due to the limited time available, the process of creating a groundwater flow model had to be hurried. Development of a more accurate groundwater flow model is desirable to increase the credibility of the transport model. The following factors may be included in further development of the groundwater flow model:

- *Sea level fluctuations*. Domsjö industrial site is located adjacent to Örnsköldsvik Bay and the groundwater conditions are likely to be affected by changes in sea level. Loggers that register pressure (groundwater level) were installed to groundwater wells in the end of March but the result from these loggers were not available when completing this study. For the areas closest to the sea, changes in sea levels are presumed to influence groundwater levels to a great extent. This means that leaching of contaminants to the bay probably is affected by sea level fluctuations. For further investigations and development of a realistic transport model these fluctuations have to be included in the model. Remediation techniques like active barriers are planned to be installed somewhere in areas C3, C5 and/or C6. Material in these active barriers may be affected when sea levels are high and sea water flows towards land causing retained contaminants in the active barrier to be brought back into the area.

- *Spatial distribution of hydraulic conductivity in the three soil type layers.* A better estimation of how the hydraulic conductivity varies throughout the soil would show a more representative picture of the groundwater conditions at the site.

The work with construction of a transport model for organic contaminants with the mobility equation and K_{DOC} values at Domsjö industrial site has only begun and requires more work before completely finished. The following proposals should be taken in consideration for further development of the contaminant transport model:

- *Site and contaminant specific constants.* A crucial factor for the predictability of the transport model is to have representative input parameters to the mobility equation. Newer measurements of especially C_s but also, if possible, measured values of K_{DOC} in the actual soil at the site are desirable.
- *DOC and contaminant degradation and retardation.* Supplying information of DOC and contaminant degradation and retardation in the soil are complex processes but will

most certainly improve the contaminant transport model and should be included for further development of the model.

- *Sensitivity analysis of model parameters*. A sensitivity analysis of all model parameters, especially of the input parameters to the mobility equation, would provide information about which parameters have most effects on the results. These are parameters most sensitive to noise. It would be useful to have such knowledge when calibrating the model.
- *Other organic contaminants.* Generally, DOC content in groundwater at Domsjö industrial site was high. Other organic contaminants such as PCB, DDT and dioxines present at higher concentrations at the site (Sweco, 2008), not studied in this thesis, are all likely to partition to DOC and transport with groundwater to the recipients River Moälven and Örnsköldsvik Bay. Other organic contaminants should therefore also be included for further investigations and development of suitable remediation techniques.

7 CONCLUSIONS

The minimum and the median value of K_{DOC} showed best modeled phenanthrene concentration compared to measured values after six years. Best result of modeled concentrations of DEHP was obtained with K_{DOC} calculated from K_{OC}. Comparison between best model simulation results of tabulated and calculated K_{DOC} values could not be made. For comparison, the tabulated and calculated K_{DOC} should be available for one single contaminant. The modeling results come with uncertainties due to estimation of site and contaminant specific constants as input to the mobility equation. For further development of the transport model, at least newer measurements of C_s are needed. Also measured values of K_{DOC} would be desirable for construction of a representative transport model.

Although the groundwater at Domsjö industrial site was characterized by phenanthrene and DEHP concentration below guideline values, at the groundwater sampling points where the contaminants were present in highest concentration, also DOC was present in highest concentration. DOC concentration in all sampling points was relatively high. Correlation analysis of DOC and contaminants showed a significant correlation for DOC and phenanthrene at 99% confidence level, and for DOC and DEHP at 90% confidence level.

Due to the persistency and toxicity of phenanthrene, DEHP and also other organic contaminants, prevention of contaminant transport is essential to avoid negative impacts on aquatic ecosystems. Clearly, DOC has an important role for transport of HOCs in the groundwater. By understanding these transport processes better, development of transport models and suitable remediation techniques is enhanced.

8 REFERENCES

Anderson, M. P. & Woessner, W. W. (1992). *Applied Groundwater Modeling: Simulation of Flow and Advective Transport.* Academic Press Inc. San Diego.

Bernes. (1998). *Persistent Organic Pollutants – A Swedish View of an International Problem*. Swedish Environmental Protection Agency. Coronet Books Inc. Värnamo.

Borg, E. & Westerlund, J. (2012). *Statistik för beteendevetare*, 3rd ed. Liber AB. Malmö.

Brooke, D. Nielsen, I. de Bruijn, J. & Hermens, J. (1990). An interlaboratory evaluation of the stir-flask method for the determination of octanol-water partition coefficients (log P_{ow}). *Chemosphere*, Vol. 21, No. 1: 119 – 133.

Burkhard, L. P. (2000). Estimating Dissolved Organic Carbon Partition Coefficients for Nonionic Organic Chemicals. *Environmental Science & Technology*, Vol. 34, No. 22: 4663 – 4668.

Chiou, C. T. (2002). *Partition and Adsorption of Organic Contaminants in Environmental Systems.* John Wiley & Sons, Inc. Hoboken, New Jersey.

Christensen, J. J. Hansen, L. D. & Izatt, R. M. (1975). *Handbook of Proton Ionization Heats.* John Wiley & Sons. New York.

County Administrative Board of Västernorrland. (2011). *Regionalt program för arbete med förorenade områden i Västernorrlands län 2012-2014.* Härnösand. Available: http://www.lansstyrelsen.se/vasternorrland/SiteCollectionDocuments/Sv/publikationer/rapporter/2011/regionalt-program-for-arbete-med-fororenade-omraden-i-vasternorrlands-lan-2012-2014.pdf. Retrieved 2013-02-19.

DHI-WASY GmbH. (2012). *FEFLOW 6.1, Finite Element Subsurface Flow & Transport Simulation System, User Manual*. DHI-WASY GmbH. Berlin.

Domsjö Fabriker. (2013). *Historik*. Available: http://www.domsjoe.com/. Retrieved: 2013-02-18.

European Union. (2007). Directive 2006/118/EC. Protection of groundwater against pollution. Available: http://europa.eu/legislation_summaries/environment/water_protection_management/l28139_en.htm. Retrieved: 2013-05-04.

Frankki, S. (2006). *Association of Organic Compounds to Dissolved and Particulate Natural Organic Matter in Soils.* Doctoral Thesis No. 2006:52. Swedish University of Agricultural Sciences. Faculty of Forest Sciences. Umeå. ISBN 91-576-7101-X.

Grip, H. & Rodhe, A. (1994). *Vattnets väg från regn till bäck*, 3rd ed. Hallgren & Fallgren Studieförlag AB. Stockholm.

Hazardous Substances Data Bank. (2013). *Database.* Available: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB. Retrieved: 2013-02-07.

Howard, P. H. (1989). *Handbook of Environmental Fate and Exposure Data for Organic Chemicals – Volume 1. Large Production and Priority Pollutants.* Lewis Publishers, Chelsea, MI.

Howard, P. H. Banerjee, S. & Robillard, K. H. (1985). Measurement of water solubilities, octanol/water partition coefficients and vapor pressures of commercial phthalate esters. *Environmental Toxicology Chemistry*, Vol. 4, No. 5: 653 – 661.

Hullberg & Hedlund. (2008). *Övervakning av prioriterade miljöfarliga ämnen listade i Ramdirektivet för vatten*. Swedish EPA report 5801.

IARC. (2000). *Di(2-ethylhexyl) phthalate*. Vol. 77, p. 41.

Inamdar, S. Finger, N. Singh, S. Mitchell, M. Levia, D. Bais, H. Scott, D & McHale, P. (2012). Dissolved organic matter (DOM) concentration and quality in a forested mid-Atlantic watershed, USA. *Biogeochemistry*, Vol. 108, No. 1 – 3: 55 – 76.

Karickhoff, S. W. Brown, D. S. & Scott, T. A. (1979). Sorption of hydrophobic pollutants on natural sediments. *Water Resources,* Vol. 13, No. 3: 241 – 248.

KIFS 2004:7. *Föreskrifter om ändring av Kemikalisinspektionens föreskrifter (KIFS 1994:12) om klassificering och märkning av kemiska produkter*. KIFS 2004:7.

Knutsson, G. & Morfeldt, C-O. (2002). *Grundvatten – teori & tillämpning*, 3rd ed. AB Svensk Byggtjänst. Stockholm.

Kresic, N. (2007). *Hydrogeology and Groundwater modeling*, 2nd ed. CRC Press, Taylor & Francis Group. Boca Raton.

Larsson, M. (2003). *Hydrogeologiska transportprocesser och modeller för föroreningsspridning*. FOI-R- -0830- -SE.

Loh, C. & Andersson Ovuka, M. (2005). *Litteraturstudie av prioriterade ämnen - Information om prioriterade ämnen listade i bilaga 10 till ramdirektivet för vatten*. Enviro Planning AB.

Miljömål. (2012). *Hur miljön mår och hur arbetet med Sveriges miljömål går*. Available: http://www.miljomal.se/. Recieved: 2013-05-03.

Montgomery, J. H. (2007). *Groundwater Chemicals Desk Reference*, 4th ed. CRC Press, Taylor & Francis Group. Boca Raton.

Neely, W. B. & Blau, G. E. (1985). *Environmental Exposure from Chemicals.* Vol. 1. CRC Press. Boca Raton, FL.

Nilsson, P. (2009). *Polycykliska aromatiska kolväten (PAH) i jord – inverkan av organiskt material och kolloidrelaterade företeelser*. University of Gothenburg. Department of Earth Sciences.

Odabasi, M. Cetin, B. & Sofuoglu, A. (2006). Henry’s law constant, octanol-air partition coefficient and subcooled liquid vapor pressure of carbazole as a function of temperature:

Application to gas/particle partitioning in the atmosphere. *Chemosphere*. Vol. 62, No. 7: 1087 – 1096.

Persson, Y. (2007). *Chlorinated Organic Pollutants in Soil and Groundwater at Chlorophenol-Contaminated Sawmill Sites.* Doctoral Thesis. Department of Chemistry, Environmental Chemistry, Umeå University. ISBN 978-91-7264-251-5.

RIVM. (2001). *Ecotoxicological Serious Risk Concentrations for soil, sediment and (ground)water: updated proposals for first series of compounds.* RIVM report 711701 020.

SMHI. (2001). *Temperaturen och nederbörden i Sverige 1961-1990. Referensnormaler - utgåva 2.* Meteorologi, 99.

SMHI. (2013). *Vattenwebb*. Available: http://vattenwebb.smhi.se/. Retrieved: 2013-02-13.

Svenskt Vatten. (2004). *Dimensionering av allmänna avloppsledningar, publication P90.* ISSN 1651-4947.

Sweco. (2008). *Domsjö industriområde, fördjupad förstudie av föroreningar i mark, grundvatten och sediment.* Sundsvall.

Swedish EPA. (2007a). *Datormodeller för föroreningsspridning fas 2*. Report 5676. Hållbar Sanering.

Swedish EPA. (2007b). Triclosan, DEHP och klordan – samlad utvärdering av svenska miljöövervakningsdata.

Swedish EPA. (2009a). *Förslag till genomförande av direktiv 2008/105/EG om miljökvalitetsnormer inom vattenpolitikens område, Redovisning av ett regeringsuppdrag*. Report 5973.

Swedish EPA. (2009b). *Riktvärden för förorenad mark*. Report 5976.

Tóth, J. (1963). A theoretical analysis of groundwater flow in small drainage basins. *Journal of Geophysical Research*. Vol. 68, No. 16. 4795-4812.

Tysklind, M. (2011). *Alternativ miljöteknik för förorenad mark med pågående verksamhet – ett FoU-projekt med fokus på Domsjö industriområde i Örnsköldsvik*. Fas I. Umeå universitet.

US Geological Survey. (2013a). *Organic matter in groundwater*. Available: http://water.usgs.gov/ogw/pubs/ofr0289/ga_organic.htm. Retrieved: 2013-02-28.

US Geological Survey. (2013b). *Octanol-Water Partition Coefficient* (*K_{OW}*). Available: http://toxics.usgs.gov/definitions/kow.html. Retrieved: 2013-03-13.

USA EPA. (2012). *Phenanthrene.* Available: http://www.epa.gov/osw/hazard/wastemin/minimize/factshts/phenanth.pdf. Retrieved: 2013-05-05.

WHO. (2003). *Di(2-ethylhexyl)phthalate in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality*. WHO/SDE/WSH/03.04/29. Available: http://www.who.int/water_sanitation_health/dwq/chemicals/di2ethylhexyphthalate.pdf. Retrieved: 2013-04-08.

WHO. (2010). *Persistent Organic Pollutants: Impact on Child Health*. Available: http://whqlibdoc.who.int/publications/2010/9789241501101_eng.pdf. Retrieved: 2013-01-24.

8.1 PERSONAL COMMUNICATION

Ylva Persson, Environmental Consultant, WSP Group. 28 February 2013.

APPENDIX A – GROUNDWATER RECHARGE

Annual precipitation data, P = 634 mm/y, for Domsjö industrial site was taken from SMHI (2001) estimated for Örnsköldsvik area. The run-off at the site, R, was estimated to 410 mm/y for SMHI watershed ID number 702282-164700 (SMHI, 2013). Evaporation was calculated to 224 mm/y with water balance equation A1, change in storage ΔS was estimated to zero.

$$R = P - E - \Delta S \qquad \text{(A1)}$$

where R is runoff [mm/y], E is evapotranspiration [mm/y] and P is precipitation [mm/y].

At Domsjö industrial site 60% of the surface area is covered by green areas, mainly grass, while 40% consists of asphalt or roofs (calculated in ArcMap 10.1). Contribution of surface run-off from each surface (green areas, asphalt and roofs) was calculated with equation A2.

$$R_{surface\ x} = \varphi_{surface\ x} \cdot P \qquad \text{(A2)}$$

Where φ is the run-off coefficient [-].

Run-off coefficient, run-off, recharge and area of green areas, asphalt and roofs is described in Table A1.

Tabell A1. Run-off coefficents, calculated run-off and recharge and surface area of green areas, asphalt and roofs at Domsjö industrial site.

	Green areas	**Asphalt**	**Roofs**
Run-off coefficient φ [-]	0.15[a]	0.8[a]	0.9[a]
Run-off [mm/y]	95	507	571
Recharge [mm/y]	315	0	0
Area [m^2]	225 580[b]	-	-
Recharge [m^3/y]	71035	-	-

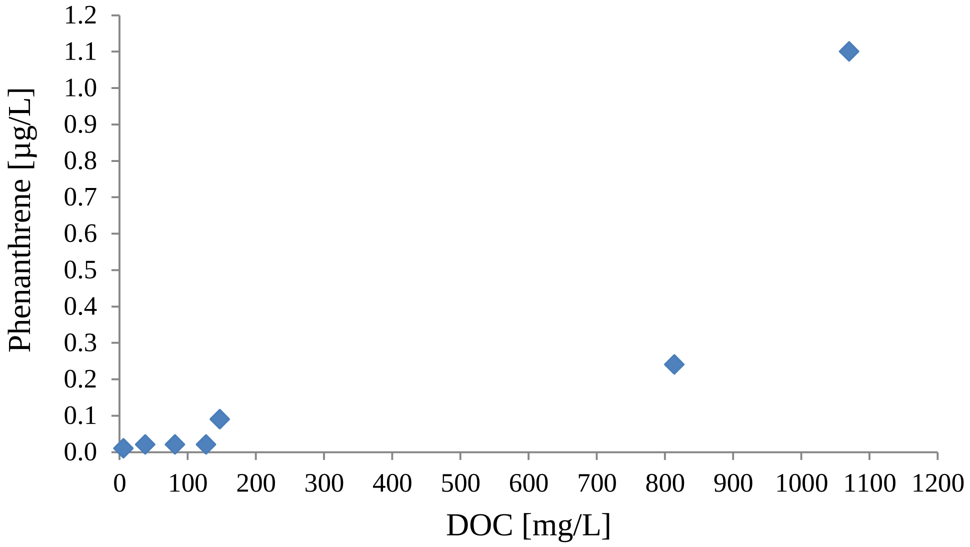
[a] Svenskt Vatten, 2004.

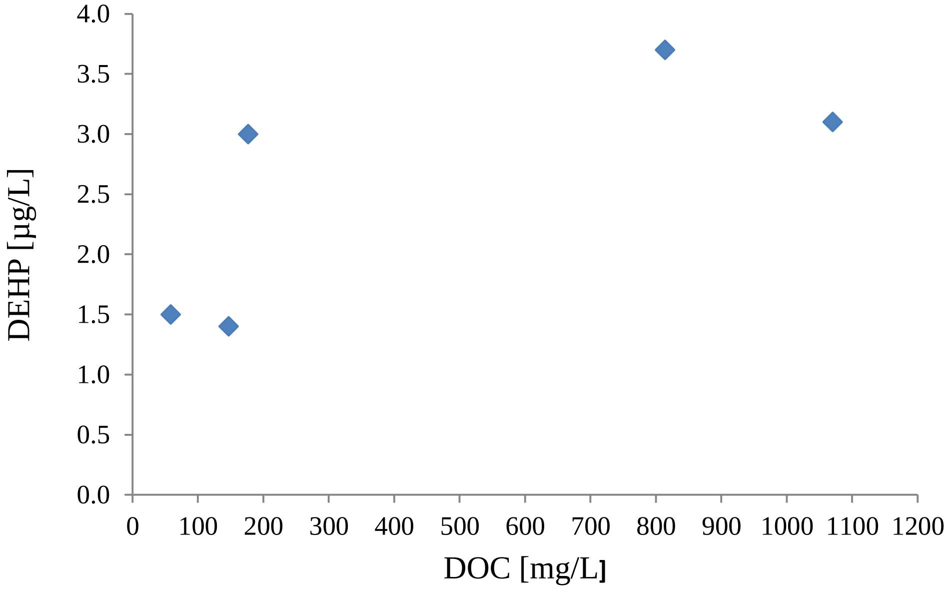
[b] Estimated with ArcMap 10.1

Mean groundwater recharge of Domsjö industrial site was calculated to 0.187 m/y = $5.14 \cdot 10^{-4}$ m/d with equation A3. There was, naturally, no contribution of groundwater recharge from asphalt and roofs. Total surface area (A_{tot}) of the model was estimated in ArcMap 10.1 to 378922 m^2.

$$Mean\ recharge = \frac{A_{green\ areas} \cdot (P - E - R_{green\ areas})/1000}{A_{tot}} \qquad \text{(A3)}$$

APPENDIX B – CONTAMINANT/DOC PLOT





APPENDIX C – MODELED C_{w_mob} VERSUS MEASURED C_{w_mob}

Scenario 1

Simulation of phenathrene concentration after six years with minimum K_{DOC} value = 8128.3 L/kg shows an under-estimation of phenanthrene concentration in the seven observation points with detectable measured phenanthrene concentration (C1). The slope of the regression line was 0.4353. Simulation was performed with 118 time step iterations and total mass rate budget was -4.3.

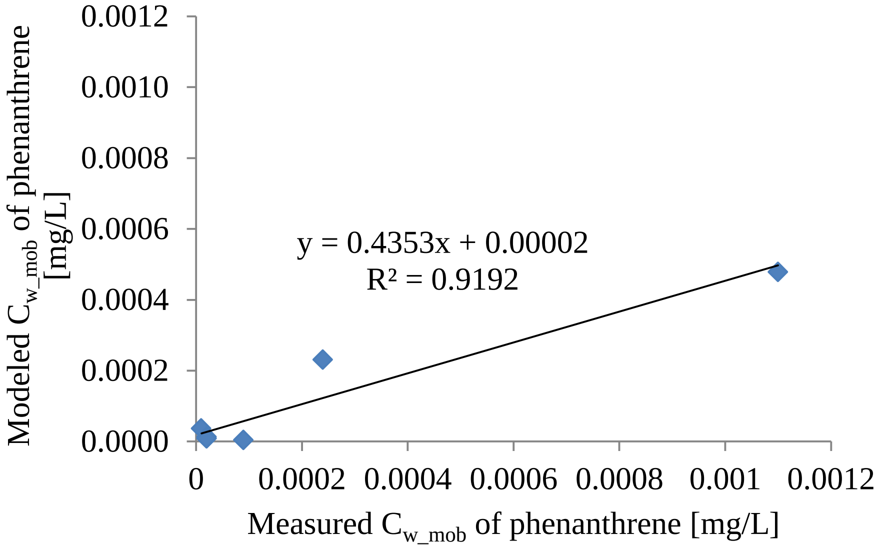


Figure C1. Modeled C_{w_mob} of phenanthrene with K_{DOC} min after six years plotted to measured C_{w_mob} shows an under-estimation of modeled C_{w_mob}.

Scenario 2

Simulation of phenanthrene concentration after six years with maximum K_{DOC} value = 3162277.7 L/kg shows an average over-estimation of phenanthrene concentration in the seven observation points with detectable measured phenanthrene concentration (Figure C2). The slope of the regression line was 26.122. Simulation was performed with 129 time step iterations and total mass rate budget was -656.

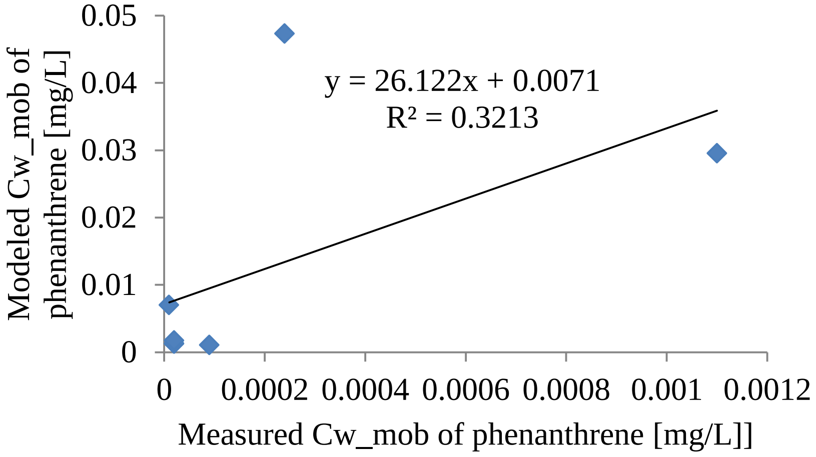


Figure C2. Modeled C_{w_mob} of phenanthrene with K_{DOC} max after six years plotted to measured C_{w_mob} shows an over-estimation of modeled C_{w_mob}.

Scenario 3

Simulation of phenanthrene concentration after six years with median K_{DOC} value = 32359.4 L/kg shows an average over-estimation of phenanthrene concentration in the seven observation points with detectable measured phenanthrene concentration (Figure C3). The slope of the regression line was 1.5057. Simulation was performed with 121 time step iterations and total mass rate budget was -9.5.

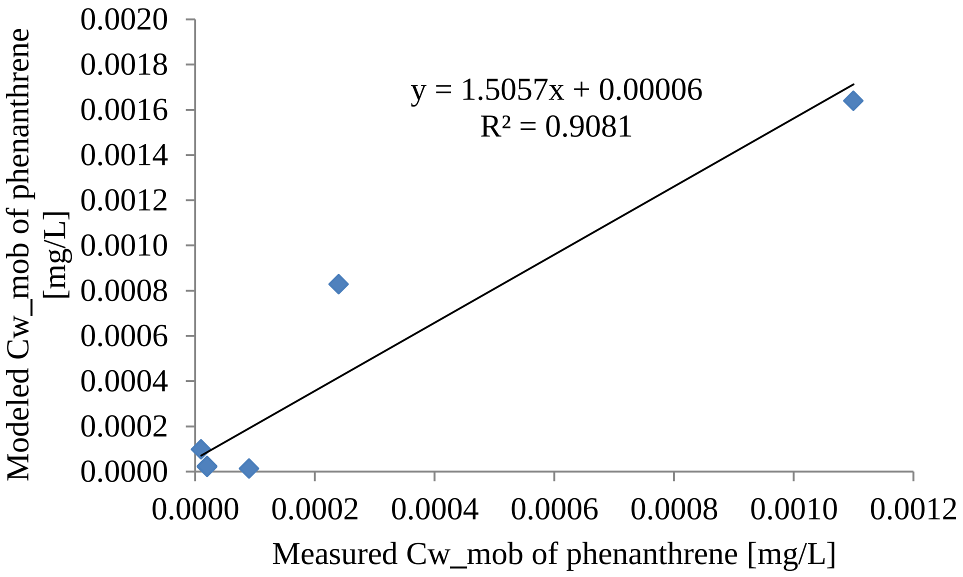


Figure C3. Modeled C_{w_mob} of phenanthrene with K_{DOC} median after six years plotted to measured C_{w_mob} shows an over-estimation of modeled C_{w_mob}.

Scenario 4

Simulation of DEHP concentration after six years with K_{DOC} value = 2400 L/kg calculated with K_{oc} shows an under-estimation of DEHP concentration in the five observation points with detectable measured DEHP concentration (Figure C4). The slope of the regression line was 0.9568. Simulation was performed with 51 time step iterations and total mass rate budget was -0.85.

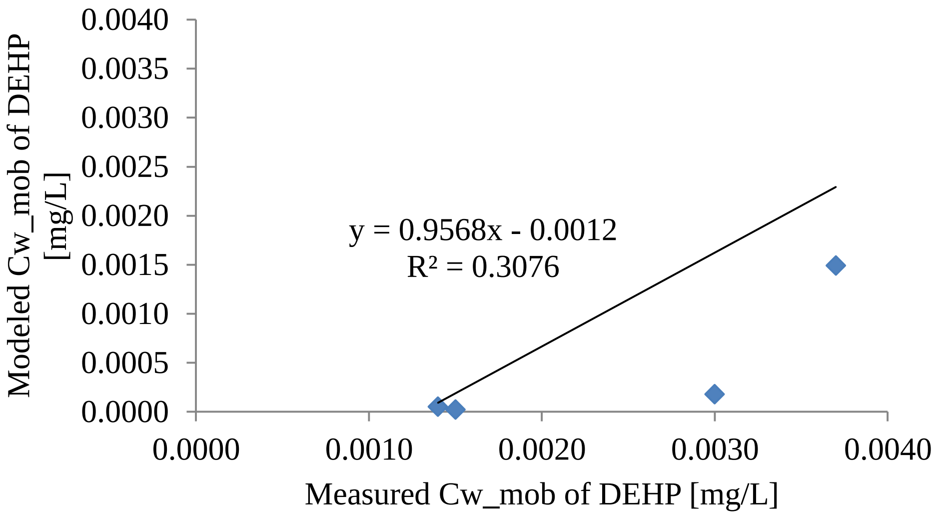


Figure C4. Modeled C_{w_mob} of DEHP with K_{DOC} calculated with K_{oc} after six years plotted to measured C_{w_mob} shows an under-estimation of modeled C_{w_mob}.

Scenario 5

Simulation of DEHP concentration after six years with K_{DOC} value = 1096705.4 L/kg calculated with K_{OW} shows an over-estimation of DEHP concentration in the five observation points with detectable measured DEHP concentration (Figure C5). The slope of the regression line was 25.242. Simulation was performed with 48 time step iterations and total mass rate budget was -38.

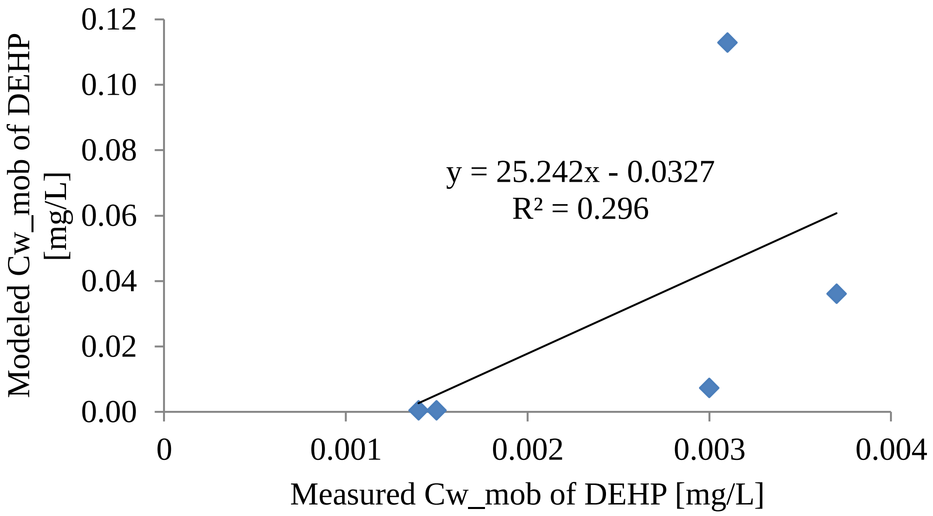


Figure C5. Modeled C_{w_mob} of DEHP with K_{DOC} calculated with K_{oc} after six years plotted to measured C_{w_mob} shows an over-estimation of modeled C_{w_mob}.