

# **Remediation of landfill leachate with an adsorption drain**

**July 5th, 2010**



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# **Remediation of landfill leachate with an adsorption drain**

**Organic material as adsorbent in an adsorption drain**



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## Responsibility

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## Colophon

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5. Recommendations for future column experiments
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## Samenvatting

Tot aan de jaren 70 (en in sommige landen gebeurt dit nog steeds) werd er in Nederland onzorgvuldig omgegaan met giftig chemisch afval en werd het vaak in stortplaatsen bedoeld voor huishoudelijk afval 'ondergebracht'. Deze onzorgvuldigheid heeft geleid tot vele bodemverontreinigingen die een ecologisch en humaan risico vormen voor de directe omgeving. Tegenwoordig zijn overheden en bedrijven in Nederland dan ook verplicht om dergelijke historische verontreinigingen aan te pakken. Veelal worden voor chemische stortplaatsen dure, niet duurzame technieken toegepast, zoals afvalmining (afgraven, scheiden en elders storten of verbranden) of volledig isoleren.

In deze studie wordt de haalbaarheid en efficiëntie van een drainerende sloot onderzocht voor de sanering ofwel stabilisering van een grondwater verontreiniging, in dit geval afkomstig uit chemisch stortmateriaal. Essentieel voor dit onderzoek is de toegevoegde waarde die organisch materiaal (veen of groencompost) kan leveren in dit saneringsconcept, genaamd de adsorptiesloot. Deze techniek zal een duurzame en kosteneffectieve oplossing kunnen vormen voor locaties waar andere technieken te kostbaar blijken te zijn.

Voor dit onderzoek zijn doorlatendheid (kolom) en adsorptie (batch) experimenten uitgevoerd op vijf typen veen en groencompost. Uiteindelijk zijn veen type 05 en groencompost geselecteerd voor verder onderzoek, omdat deze materialen de hoogste potentie leken te hebben voor de adsorptiesloot. Met deze materialen zijn opnieuw adsorptie experimenten uitgevoerd in zowel batches als kolommen. Benzeen is geselecteerd als verontreiniging, omdat dit veelal een kritieke stof in grondwaterpluimen is (ook in het betreffende stortpercolaat in Zeeland) en dus een belangrijke rol speelt voor het succes van de adsorptiesloot.

Uit de resultaten van de kolom en batch experimenten is voor veen 05 een retardatie factor variërend tussen de 3,84 en 4,9 gevonden. Dit komt overeen met een  $K_d$  waarde tussen de 22,9 en 31,1 l/kg voor de adsorptie van benzeen aan veen 05. De retardatie factor en  $K_d$  waarde voor groencompost lieten een grotere variatie zien, omdat benzeen een hogere adsorptie bleek te hebben tijdens de kolom experimenten. Een retardatie factor tussen de 2,84 en 4,4 is gevonden voor groencompost, wat overeenkomt met een  $K_d$  waarde tussen de 3,49 en 6,45 l/kg.

Een MODFLOW grondwater model is gebruikt voor het uitvoeren van een gevoeligheidsanalyse betreffende de werking van de adsorptie sloot. Vooral de interceptie diepte van de sloot en de verblijftijd van grondwater in de sloot zijn belangrijke eigenschappen voor de sanerende werking. Het doel van het model was het aantonen van de invloed van verschillende hydrologische parameters op deze eigenschappen. Uiteindelijk is gebleken dat de weerstand van de

drainbodem en de mate van drainafvoer vooral de verblijftijd beïnvloeden. De natuurlijke grondwaterflux is daarnaast de belangrijkste factor wat betreft interceptiediepte voor een specifieke drainage afvoer.

De rol van biodegradatie in de adsorptiesloot wordt in dit verslag slechts benoemd en ingeschat. Toekomstig onderzoek zal moeten uitwijzen of organisch materiaal, toegepast zoals in de adsorptiesloot, biodegradatie (zowel in het adsorptiemateriaal als het oppervlaktewater) kan stimuleren.

Over het algemeen kan geconcludeerd worden dat de haalbaarheid en efficiëntie van een sanering met behulp van een adsorptiesloot voornamelijk afhangt van de lokale hydrologische- en verontreinigingssituatie. Vooral ondiepe verontreinigingen in langzaam stromend grondwater zijn wenselijk wanneer een dergelijk systeem wordt toegepast. Dit betekent namelijk dat de afvoer van de sloot laag gehouden kan worden wat de levensduur van het organische materiaal als adsorptiemedium ten goede komt. Benzeenretardatie voor de onderzochte materialen blijkt daarnaast lager te zijn dan verwacht. Bij groencompost wordt dit waarschijnlijk veroorzaakt door het lage organisch koolstofgehalte en het lage specifieke oppervlak. Voor veen speelt de lage dichtheid een beperkende rol, waardoor er relatief weinig organische stof per volume aanwezig is. Voor stoffen met een hogere verdelingscoëfficiënt dan benzeen zal de adsorptiecapaciteit en daarmee de levenscyclus van veen als adsorptiemedium overigens hoger liggen.

## Abstract

Until the seventies storage of toxic pollutants in The Netherlands was (and in some countries still) done carelessly. The chemicals were often dumped in landfills which were designed for domestic waste. This carelessness has led to many soil contaminations which form ecological and human risks for the direct environment. Nowadays, governments and companies are therefore obliged to remediate such historic contaminations. Remediation of chemical landfills is often done with unsustainable techniques such as, wastemining (excavation, sorting and relocating or incinerating) or complete isolation.

In this study the feasibility and efficiency of a draining trench for the remediation or stabilization of a groundwater contamination, in this case from a chemical landfill, is studied. Essential for this study is the value which organic material (peat or green compost) could add to this remediation concept, named the adsorption drain. This technique could form a sustainable and cost effective solution for locations where other techniques prove to be too expensive.

For this research, hydraulic conductivity (column) and adsorption (batch) experiments have been done on five types of peat and green compost. Peat type 05 and green compost were selected for further research, because these materials seemed to have the highest potential for application in the adsorption drain (trench). Additional adsorption experiments (batch and column) were conducted on the materials. Benzene was selected as contaminant, because benzene is a critical pollutant in groundwater plumes (also in the landfill leachate of Zeeland). Benzene is therefore a determining pollutant for the success of the adsorption drain.

From the results of the column and batch experiments a retardation factor between 3.84 and 4.9 is found for peat 05. This corresponds to a  $K_d$  value between 22.9 and 31.1 l/kg for adsorption of benzene to peat 05. The retardation factor and  $K_d$  value of green compost showed a larger variation, because benzene seemed to be more adsorbed during the column experiments. A retardation factor between 2.84 and 4.4 is found for green compost, which corresponds with a  $K_d$  value between 3.49 and 6.45 l/kg.

A MODFLOW groundwater model was used for a sensitivity analysis concerning the working of the adsorption drain. The interception depth of the trench and the residence time of groundwater in the trench are the most important properties for the remediating effect. The goal of the model was to demonstrate the influence of different hydrological parameters on these properties. It is shown that mainly the drain bed resistance and the drain discharge influence the residence time. The natural groundwater flux is the most important factor regarding the interception depth for a specific drainage discharge.

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The roll of biodegradation in the adsorption drain is only appointed and estimated in this study. Future research should show if organic material, used as in the adsorption drain, could stimulate biodegradation in the adsorption material and in the surface water.

In general it could be concluded that the feasibility and efficiency of a remediation with an adsorption drain (trench) depends mainly on the local hydrological- and contaminant situation. Shallow pollutants in slowly flowing groundwater are desirable when such a system is applied. This implies that the drainage of the trench can be low which increases the lifespan of the organic material that is used as adsorption medium. Besides that, benzene retardation for the studied materials appeared lower than expected. This is probably caused by the low specific surface and low organic carbon content of green compost and the relatively low density of peat. Relative little organic carbon per volume peat is available, due to the low density. The adsorption capacity and therefore the lifespan of organic material as adsorption medium will however be larger for contaminants with a higher partitioning coefficient than benzene.

## List of abbreviations

A	Surface area	[L <sup>2</sup> ]
C <sub>0</sub>	Initial solute concentration	[M/L <sup>3</sup> ]
C <sub>g</sub>	Concentration of contaminant in the gas phase	[M/L <sup>3</sup> ]
C <sub>e</sub>	Equilibrium concentration in solution	[M/L <sup>3</sup> ]
C <sub>f</sub>	Input solute concentration	[M/L <sup>3</sup> ]
C <sub>d</sub>	Drain conductance	[L <sup>2</sup> /T]
d <sub>0</sub>	Maximum drain water depth	[L]
d <sub>d</sub>	Drain water level during discharge	[L]
D	Capture depth of the interceptor ditch	[L]
D	Dispersion coefficient	[L <sup>2</sup> /T]
Ec	Electric conductivity	[S/L]
Ec <sub>0</sub>	Initial electric conductivity	[S/L]
Ec <sub>b</sub>	Background electric conductivity	[S/L]
Ec <sub>m</sub>	Measured electric conductivity	[S/L]
F <sub>oc</sub>	Fraction of organic carbon	[-]
F	Solute mass flux	[M/L <sup>2</sup> T]
G	Aquifer groundwater flux (K*i)	[L/T]
h	Head	[L]
H	Head difference	[L]
h <sub>0</sub>	Head in the aquifer beneath the ditch	[L]
h <sub>d</sub>	Ditch stage	[L]
H <sub>cc</sub>	Dimensionless Henry's constant	[-]
i	Hydraulic gradient	[-]
I	(Regional) water-table gradient	[-]
K	Hydraulic conductivity	[L/T]
K <sub>d</sub>	Partitioning coefficient	[L <sup>3</sup> /M]
K <sub>f</sub>	Freundlich equation parameter	[L <sup>3</sup> /M]
K <sub>oc</sub>	Organic carbon partitioning coefficient	[L <sup>3</sup> /M]
K <sub>sd</sub>	Drain vertical hydraulic conductivity	[L/T]
K <sub>x</sub>	Horizontal hydraulic conductivity	[L/T]
K <sub>y</sub>	Vertical hydraulic conductivity	[L/T]
L	Length of specimen or drain channel length	[L]
m	Thickness of the drain adsorption material	[L]
M <sub>g</sub>	Mass of contaminant in the gas phase	[M]
M <sub>s</sub>	Mass of dry soil	[M]
M <sub>w</sub>	Mass of contaminant in the water phase	[M]

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n	Freundlich equation parameter	[-]
Q	Discharge	[L <sup>3</sup> /T]
q <sub>v</sub>	Vertical groundwater flux	[L/T]
r	Anisotropy ratio (K <sub>x</sub> /K <sub>y</sub> )	[-]
R	Retardation factor	[-]
r <sub>s</sub>	Rate of sorption	[M/L <sup>3</sup> T]
S <sub>eq</sub>	Equilibrium mass of adsorbed solute per unit mass of dry soil	[M/M]
s	Mass of adsorbed solute per unit mass of dry soil	[M/M]
t <sub>c</sub>	Cumulative time	[T]
t <sub>r</sub>	Residence time	[T]
V	Volume	[L <sup>3</sup> ]
V <sub>w</sub>	Volume of water or solute	[L <sup>3</sup> ]
V <sub>m</sub>	Volume of water as moisture in material	[L <sup>3</sup> ]
V <sub>a</sub>	Volume of air	[L <sup>3</sup> ]
v <sub>cont</sub>	Contaminant flow velocity	[L/T]
v <sub>water</sub>	Water flow velocity	[L/T]
w	width of the drain channel	[L]
μ	First order decay rate coefficient	[T <sup>-1</sup> ]
θ	Porosity	[-]
θ <sub>calibrated</sub>	Calibrated porosity or effective porosity	[-]
θ <sub>e</sub>	Effective porosity	[-]
θ <sub>measured</sub>	Measured porosity or total porosity	[-]
ρ <sub>b</sub>	Bulk density	[M/L <sup>3</sup> ]
λ	First order biodegradation constant	[T <sup>-1</sup> ]

### List of dimension symbols

L	Length
M	Mass
T	time
S	Siemens

# 1 Introduction

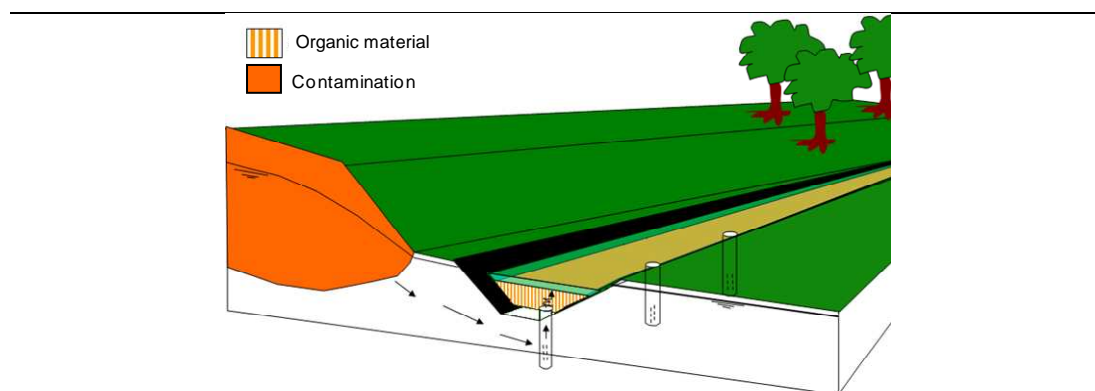
This Msc research is done in assignment of Tauw B.V. which is a European consulting and engineering company specialised in the design, improvement and management of the natural environment, built-up environment and infrastructure. Tauw is an expert and leading company in the field of environmental consultancy, spatial development, civil engineering and the monitoring of environmental quality. In these fields a prominent reputation has been acquired in studies and design.

## 1.1 Background

Since the industrial revolution, soils have been contaminated widely with toxic chemical wastes. Until the seventies these chemical wastes were not separated from domestic wastes and both were dumped in landfills. Nowadays, we realise that these chemical wastes form an ecological and environmental threat. In general the remediation of contaminated sites is often an expensive and difficult task. Several intensive techniques, such as landfill mining and physical isolation of landfills or, at other contaminated sites, excavation, pump and treat, thermal methods, and in-situ chemical oxidation have been used. The suitability of a method depends on site characteristics, chemical characteristics, and economical, environmental and risk considerations.

A well-known chemical and domestic waste dump in the Netherlands is a landfill near Amsterdam, named Volgermeerpolder. In the twentieth century, all kinds of chemical wastes have been dumped at this landfill. The site covers an area of 100 ha and 350 monitoring wells were placed around the landfill to determine the migration of the pollutants. They found that no (or little) migration of mobile organic pollutants had occurred, although migration was expected. It was concluded that in this case the underlying peat prevented the further migration of pollutants. This conclusion led to the idea to use peat or another organic material in the remediation measures of contaminated sites.

Organic material can be used in two different ways; as adsorbent in a drain or as natural cap. In the case of the natural cap, a living peat layer on top of a landfill is used to prevent human and animal contact with the chemical waste (direct contact as well as indirect contact by evaporation and or migration with rainwater). When peat is applied in this way, it is used as a living isolation material. In the case of the adsorption drain a channel is filled with organic material to control a groundwater contamination plume and/or landfill leachate. This thesis will focus on the development of an adsorption drain in which an organic material is used as adsorbent (fig. 1.1).



**Figure 1.1 Schematic drawing of the adsorption trench.**

## 1.2 Motivation

The capability of organic materials to adsorb organic pollutants is a well known fact. During migration calculations of contaminants, the retardation caused by the adsorption to organic matter in soils is always taken into account. Furthermore, activated organic carbon is often used as filter material for volatile components or in groundwater remediation. Activated organic carbon is, however, far more expensive than natural materials like peat or compost. It is however questionable whether these materials have the same effectiveness as activated carbon and/or the hydrological characteristics of the material are suitable for use in drains (trenches).

The (passive) adsorption drain could be a cost effective alternative for the remediation and management of landfills. It has therefore a high potential in development countries, where lots of (chemical) landfills are present and often no money is available for intensive remediation techniques. But also for sites in developed countries where other techniques are economically or environmentally not favourable due to, for example, the size of the contaminated site (like large landfills) and/or health and safety risks.

## 1.3 Objectives and research questions

The main objective of this thesis is to study the applicability of an adsorption drain for the control of groundwater contaminated plumes, in particular for a landfill site in Zeeland. The other objectives are:

- Find the most applicable organic material for the adsorption drain.
- Find out which mechanisms contribute to the filtering capacities of organic material.

These objectives led to the following research questions which will be addressed in this thesis:



- Which available organic material has the most potential for use in the adsorption drain?
  - regarding conductivity
  - regarding adsorption capacity
  - regarding biodegradation
- What is the durability of the organic material?
- What are the optimal dimensions of the adsorption drain?

#### **1.4 Thesis outline**

The applicability and possibility of remediation with an adsorption drain has been studied and is described in this thesis. Literature, experimental and model data are presented in chapter 2 to 6. Chapter 2 presents a literature review about remediation experiences with organic material. First an introduction to sorption of organic contaminants to organic matter is given. Thereafter, previous works wherein the adsorptive capability of peat is studied are described. Furthermore, attention is given to the potential of aerobic biodegradation in the adsorbing material of the drain and some case studies which have looked into organic material in contaminant barrier systems. A literature review of hydrological factors, which play an important role in the success of the drain, is given in chapter 3. Chapters 4 and 5 present the experimental data of the studied organic materials in the laboratory. In chapter 4, the studied organic materials and applied methods are described and in chapter 5 the results are discussed. In chapter 6 the results of a 1D modelling study are given and a field example is described. The thesis ends with a discussion and conclusion section followed by some recommendations. The recommendations are especially interesting for future studies on the potential of the adsorption drain.



## **2 Remediation with organic material – literature review**

### **2.1 Sorption to organic matter**

An organic contaminant that is dissolved in the pore water will distribute over two phases; the water and the solid phase. Sorption is the collective term which is used for absorption, adsorption, and desorption. Adsorption describes the process of a (molecular or ionic) contaminant binding to the solid matrix, while desorption is the reversed process of adsorption (dissolution into the pore water). Absorption describes the process of free product infiltrating into another medium. Both processes cause the containing of contaminant into/onto a sorbent. The focus of this section will be on adsorption (in the form of physisorption), but also some cases of absorption will be discussed.

Both adsorption and absorption occur when an organic (solid) material interacts with an organic (liquid or gaseous) contaminant. There is however a significant difference between the two processes. One form of adsorption is physisorption which is the adhesion of a contaminant to the surface of a solid phase. Physisorption is a reversible process and is valid for adsorption onto organic material or (activated) carbon. The other form of adsorption is chemisorption which is an irreversible process and consists of a chemical (reaction) bond. Physisorption is a relatively fast and reversible process, because it is a surface process and binding forces are weak. In contrast to that, chemisorption is a slow but irreversible process and to a lesser content valid for organic contaminants. In most cases physisorption is the relevant process on which chemisorption can follow. In the absorption process the free product of the contaminant will permeate into the texture of a solid phase.

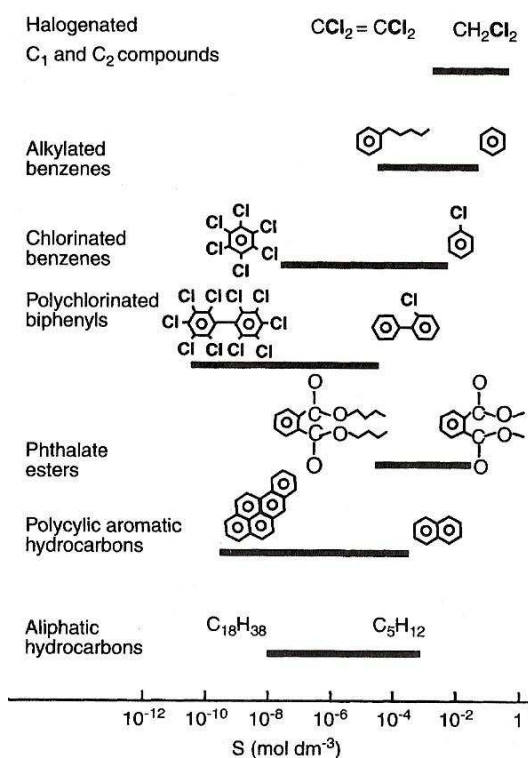
The extent of adsorption is influenced by the nature and concentration of the contaminant, and by the composition of both the groundwater and the soil matrix. The amount of organic material is a determining factor for sorption of organic contaminants. This is because the interaction between uncharged molecules (or uncharged portions of molecules) and soil humus is often stronger than the interaction between these kinds of molecules and groundwater, which results in adsorption to humus. According to Sposito (2008) this occurs for two distinct reasons. 'First, water molecules interacting with a nonpolar molecule in the soil solution are confronted by a lack of electronegative atoms with which to form a hydrogen bond, so they cannot orient their very polar OH toward the molecule in ways that are compatible with the tetrahedral coordination they engage in the bulk liquid structure. Instead, the water molecules must form a network of hydrogen bonds that point roughly parallel to the surface of the nonpolar molecule, thereby enclosing it in a

kind of cage structure (hydrophobic effect). The resultant distribution of the tetrahedral ordering in liquid water and the cost in energy to produce the anomalous cage result in a low water solubility of the nonpolar molecule. The second reason for a stronger interaction with humus is the presence of nonpolar moieties in the latter. From the perspective of minimizing disruption of the normal liquid water structure, it is optimal to have a nonpolar molecule adsorb on a nonpolar domain of humus, so that fewer water molecules are needed to accommodate to the two than when they are far apart. Although van der Waals interactions between nonpolar molecules are approximately of the same strength as those between water molecules, the gain to the latter in not having to form as extensive a cage structure produces a strong tendency for nonpolar units to bind together in the presence of liquid water (hydrophobic interaction)' (Sposito, 2008).

Sposito (2008) continues with explaining that the relationship between the hydrophobic effect and water solubility can be quantified by two important properties of uncharged molecules; the number of chlorine substituents and the solvent-excluding area. 'Chlorine is a highly electronegative atom that, upon replacing H on a carbon atom, can then withdraw significant electron charge density carbon-carbon bonds in chain or ring structures, thus rendering them less polar and more hydrophobic. Solvent-excluding area (the same as the total surface area for a nonpolar molecule) provides a measure of the size of the interface across which no hydrogen bonds cross, which is created when the hydrophobic effect occurs. This interface disrupts the structure of liquid water, leading to cage formation that is inimical to high water solubility. Figure 2.1 depicts the water solubility for several classes of organic compounds. Solubility is decreasing when either the number of chlorine substituents increases or the molecular size increases' (Sposito, 2008).

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**Figure 2.1 Ranges of water solubility for classes of organic compounds of varying hydrophobicity by increasing chlorine substitution or solvent-excluding area. (From: Schwarzenbach et al., 2003)**

Beside the presence of organic material (humus) in the soil matrix, organic material could also be dissolved into the groundwater. Dissolved organic material (DOC) consists of organic molecules, which have a high affinity with organic contaminants. Concentrations of dissolved organic matter are usually around a few mg per litre, but can rise (e.g. in a contaminant plume near a landfill) to a few hundred mg. Adsorption onto the dissolved organic matter, in contrast to adsorption onto soil organic matter, will increase the mobility of the organic contaminant (Keijzer et al., 2006).

Adsorption to a soil is often experimentally determined by batch experiments. The sorption data can be described by a variety of adsorption isotherms, namely; linear, Freundlich, Langmuir and BET. Linear sorption isotherms are often observed if the equilibrium aqueous phase organic compound concentrations are below 10<sup>-5</sup> M or one-half of the aqueous phase solubility and the organic content of the solid is greater than 0.1% (Suthersan, 2002). Other assumptions for linear adsorption are that the adsorption is reversible and that adsorption occurs on a heterogeneous surface, and to several different types of sorption sites (Keijzer et al. 2006):

$$S_{eq} = K_d C_e$$

Where  $S_{eq}$  is the equilibrium concentration adsorbed by the solid phase [M/M],  $C_e$  is the equilibrium concentration in the aqueous phase [M/L<sup>3</sup>] and  $K_d$  is the partitioning coefficient [L<sup>3</sup>/M].

If concentrations in the aqueous phase are high, the linear adsorption isotherm may lead to an overestimation of the quantities that are adsorbed to the soil matrix. In this case the Freundlich isotherm yields a better measure, which is most often used to describe a nonlinear relationship between the adsorbed ( $S_{eq}$ ) and the solution phase concentrations ( $C_e$ ):

$$S_{eq} = K_f C_e^n$$

$K_f$  is the Freundlich sorption coefficient [L<sup>3</sup>/M] and  $n$  is a constant which is a measure of the nonlinearity involved in the sorption. When adsorbed molecules hinder the sorption of additional molecules,  $n$  is smaller than one. In contrast, when  $n$  exceeds one, sorbed molecules change the surface such, that sorption is favored more, leading to better sorption of additional sorbate molecules. This situation is encountered with surface active compounds. Whenever  $n$  is equal to one, a linear equation results, and  $K_f$  and  $K_d$  are equivalent.

'The Langmuir and BET models are also used to describe nonlinear sorption behavior for environmental solids, particular for mineral dominated sorption. The Langmuir model assumes that maximum adsorption corresponds to a saturated monolayer of solute molecule on the adsorbent surface, that there is no migration of the solute on the surface, and that the energy of adsorption is constant. The BET model is an extension of the Langmuir model that postulates multilayer sorption. It assumes that the first layer is attracted most strongly to the surface, while the second and subsequent layers are more weakly held' (Suthersan, 2002).

## 2.2 Peat as adsorption medium

Peat is partially fossilized plant matter, formed in poorly oxygenated wetlands, where the rate of accumulation of plant matter is greater than that of decomposition. The major constituents of peat are lignin and cellulose. Lignin and cellulose are hydrophobic in nature due to which organic contaminants adsorbed to them (see paragraph 2.1). These properties make peat in potential a good adsorbent and peat is therefore an often studied unconventional adsorbent material.

### Absorption

A literature research showed that especially the use of peat for the extraction of oil from oil/water emulsions is an often studied principle (Smith and mark, 1976; Viraraghavan and Mathavan, 1988; Viraraghavan and Mathavan, 1989; Viraraghavan and Mathavan, 1991). Smith and Mark

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(1976) did research on modified forms of peat. They tested dried 'Irish' peat and sulphuric acid-treated 'Michigan' peat. They used an emulsion which was prepared by adding 5 ml of Exxon 260 diesel fuel (with a density of 0.84 g/ml at 24 °C) to 3.5 litre of distilled water. The coalescence capability of the peat samples in distilled and synthetic sea water were compared with a synthetic filter material. They found that the peats were capable of removing ~90% of the oil in ~250 ppm oil-in-water emulsion from a flow system at 25 ml/min, which is comparable with synthetic filters. The limitations reported were the leaching of fulvic acids from untreated peat under alkaline conditions and the effect of detergents (added to promote dispersion) which hinder coalescence.

Viraraghavan and Mathavan (1988) conducted batch and column experiments to assess the potential of Saskatchewan horticultural peat for treating various (standard mineral oil (medium viscous), midale crude oil (low viscous), cutting oil and refinery effluent) oil-in-water emulsions. Synthetic emulsions were prepared in the case of standard mineral oil and midale crude oil, by mixing a known weight of oil with tap water and decanting the floating oil after equilibrium. The cutting oil and refinery effluents where collected at a technical institute and refinery, respectively. The equilibrium time of absorption was found to be between 2 and 3 hours for the different oil dispersions. Absorption isotherms were constructed from the batches, a BET-isotherm fitted the absorption data best. The oil-binding capacity of the peat was found to be 7.5-7.8 times its weight. The column experiments showed that, in the column filled with 30 cm peat, 90% of the oil was adsorbed during an 8 hour run with a flow rate of 12 ml/min. It was concluded that the peat columns could take higher flow rates and longer filter runs. Viraraghavan and Mathavan (1989) did a comparable research to oil absorption from produced waters recovered from a petroleum contaminated site. In all cases, the floating oil was separated and the emulsified sample was used in the experiments. Langmuir and Freundlich isotherms fitted the absorption data best. They found an average oil removal of 80% in an 8 hour run with a flow rate ranging between 12 and 48 ml/min. The same authors (Mathavan and Viraraghavan, 1991) looked to the efficiency of a 100 cm peat bed to remove a standard mineral oil-in-water emulsion at six different flow rates. They found that efficiency decreased with increasing bed depth, indicating sequential action of filtration and coalescence of oil in the peat. Due to the sequential action, the sorption of larger diameter oil droplets is favourable. It is therefore questionable if highly stable oil-in-water emulsions (characterized by oil droplets with small diameters) can be treated with peat.

Bel'kevich et al. (1983) tested 'Sphagnum' peat, 'granulated bag peat', and 'cotton grass/Sphagnum' peat for their abilities to extract oil from oil-in-water emulsions under different flow rates. These peats were able to achieve an oil removal of 88-99% at rates of 5-13 ml/h and concentrations of about 0.9 mg/l (Cohen et al., 1991).

Ghaly et al. (1999) investigated a remediation process for diesel-contaminated soil, in which water was used to remove the diesel from the soil and peat was used to absorb the diesel layer

formed on the surface of the water. They found a peat-diesel absorption capacity ranging from 3.27 to 4.9 its weight.

### Adsorption

Peat was also used to remove pentachlorophenol from wastewater. Viraraghavan and Tanjore (1994) showed that 91% of PCP was removed from municipal wastewater spiked with approximately 1 mg/L of PCP, with an equilibrium time of five hours. The peat was oven dried at 103°C for 24 hours, prior to being used for batch experiments. The adsorption was pH dependent and optimal results were found at a pH range of 3.0-3.5. This result suggested that PCP in its molecular form was readily adsorbed. The lower adsorption at higher pH, when PCP is present in its anionic form, can be explained by the high cation exchange capacity of peat. Adsorption remained approximately constant at pH below 3. In their experiments they used 0.5 gram of peat for all initial concentrations. They found that the area available for adsorption at high initial concentrations was lower than with lower initial concentrations. This effect caused adsorption to be relatively higher at low initial concentrations, which indicate adsorption to the macropore surface of peat. As the initial concentration of PCP increases, relatively less PCP will find surface area to adsorb on. They conclude that the Freundlich isotherm fitted the data best, which suggests that the adsorption process may be due to physical adsorption (physisorption instead of chemisorption) of the PCP molecules to the peat surface.

There have been numerous studies to the applicability of peat as adsorbent. Novoselova and Sirotkina (2008) did a literary review in which modified forms of peat are discussed. They concluded that especially the thermal treatment of peat at temperatures lower than 300-340 °C had a large effect on sorption capacity. This was caused by the decrease in moisture content, due to which the hydrophobicity and thus the sorption capacity was increased. A further increase in temperature resulted however in the decrease of oil capacity of peat. According to the authors this was due to intense decomposition and carbonization processes in the organic peat material.

In the past Tauw bv did a laboratory research on the potential of peat as adsorbent for leaching pollutants out of dredging sludge depots (Urlings et al., 1986). Urlings et al. (1986) did batch experiments on a mix of relatively highly adsorbing chemicals (nonane, hexadecane, benzo(b)fluoranthene, benzo(a)pyrene, trichlorobiphenyl, hexachlorobiphenyl, hexachlorobenzene, pentachlorophenol and alpha, beta- and gamma-hexachlorocyclohexane) with two types ('Klazienaveen' and 'Ermelo') of peat and a clay as adsorbents. A worst case scenario (nonane) was deduced from the results ( $K_{oc} = 500 \text{ dm}^3/\text{kg}$ ,  $q_v = 50 \text{ mm/year}$ ). The maximum infiltration velocity of the contaminants over a period of 100 years was calculated from this. For peat this was found to be 0.16 cm/year ( $f_{oc} = 0.5$ ) and for clay 0.41 cm/year ( $f_{oc} = 0.025$ ). A column test was



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recommended to determine whether high loading of contaminants will cause breakthrough of the adsorbents. During batch experiments breakthrough was not observed.

The possibility to treat a creosote-contaminated groundwater with a peat/sand permeable barrier under aerobic conditions was investigated with a column study by Rasmussen et al. (2002). Creosote-contaminated water (sterile and non-sterile) was applied to sterile and non-sterile saturated columns with 20% peat and 80% sand for 2 months. Temperature was 9 °C, inlet oxygen concentration 9-10 mg/l and average residence time was two days. From the sterile column they found that especially naphthalene (62%), PAHs (3-6 rings) (90%), two-ring nitrogen/sulfer/oxygen (NSO)-compounds (65%) and three-ring NSO-compounds (94%) were adsorbed by the peat. Phenol and cresols (0%), dimethylphenols (9%) and trimethylphenols (36%) were adsorbed to a lesser extent. Rasmussen et al. (2002) gives no reason for the difference in adsorption, but it is probably caused by the difference in solubility and therefore hydrophobicity (polarity) of the different contaminants. The non-sterile columns showed that non-adsorbed fractions of the contaminants could be efficiently degraded under aerobic conditions, which was verified by degradation measurements without adsorption material. It was concluded that sorption was the major removal process, but it also makes the compounds unavailable for microorganisms, hence, sorption sites are filling up. Therefore, a two-zone barrier system is suggested in order to enhance biological removal; the first zone contains minimum of organic material such that the compounds are bioavailable for aerobic degradation, and the second zone contains sufficient organic material to adsorb or further degrade the creosote compounds (Rasmussen et al., 2002).

Cohen et al. (1991) investigated the effect of differences in the chemical and physical composition on their ability to extract volatile hydrocarbons (benzene, xylene and toluene) from water. The purpose of their project was to test the hypothesis that peats of different composition have different potentials to extract hydrocarbons from water (either in the free-phase state or in saturated solution). An additional goal was to establish whether any parameters of peat composition could be found to correlate with hydrocarbon removal. Especially, the removal of dissolved contaminants was not investigated before; while these are the standard contaminants measured in groundwater that has become contaminated by leakage from, for example, underground gasoline storage tanks. This research is in the scope of underlying research in which the focus is also on dissolved contaminants. Cohen et al. (1991) found that in the free-phase experiment the type of hydrocarbon was not a factor of importance on the absorbencies exhibited by a specific peat type. This was in contrast to what they found for the solution experiments (in which **adsorption** took place instead of **absorption**). All peats tended to absorb the free-phase hydrocarbon to some degree, extraction ranged from 30 to 50% of the starting wet volume of the peats. Less adsorption was however found for the Maine Sphagnum peat (fig. 2.2). This peat has a high degree of fibre preservation, a high water-holding-capacity and a relatively

high microscopically measured porosity. Pore size, type and shape could be significant factors but these parameters were not measured. However, pore size is visibly larger in the Sphagnum peat than in the other types (Cohen et al., 1991).

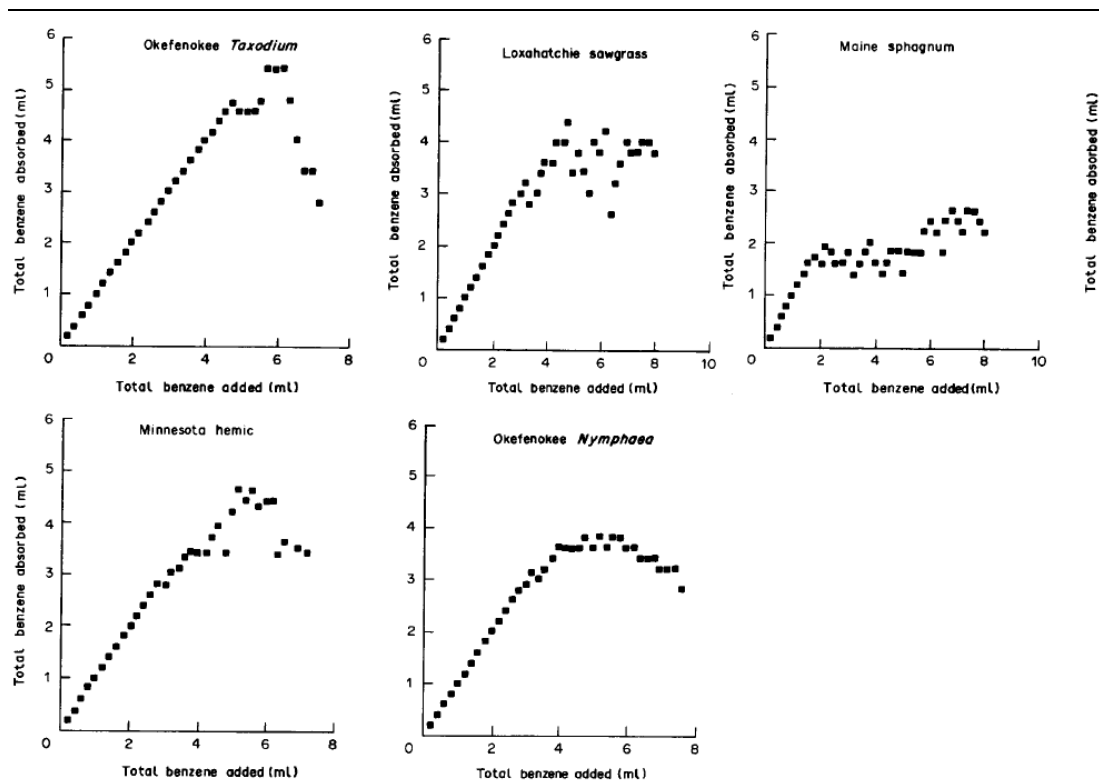


Figure 2.2 Capacities of peats of different type to absorb free-phase benzene from water (from: Cohen et al., 1991).

The 24 hour solution batch experiments of Cohen et al. (1991) showed that all peat types adsorbed significant amounts of the hydrocarbons from solution (63-97% of the standard, figure 2.3). It is shown that benzene and xylene exhibit somewhat similar trends with regard to the adsorbencies of the peat types. Toluene took longer to be adsorbed and therefore a 12 day experiment was conducted on toluene. This is peculiar, because properties of toluene are between the properties of benzene and xylene, and xylene does not adsorb different from benzene. The time to adsorb is an important factor for the design of a remediation system.

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	Okefenokee <i>Taxodium</i>	Peat type Loxahatchee <i>Nymphaea</i>	Minnesota hemic	Loxahatchee sawgrass	Okefenokee <i>Nymphaea</i>	Maine sphagnum
<i>Benzene 24 h results</i>						
Amount remaining in solution (mg/g)	0.133	0.367	0.409	0.452	0.463	0.587
Amount sorbed (percent of standard)	93	79	77	75	74	67
Sorption capacity (mg/g organic carbon)	26.8	33.6	24.5	33.2	30.3	36.2
$k_{oc}$	201	91.7	59.9	73.5	65.4	61.6
$\log k_{oc}$	2.30	1.96	1.78	1.87	1.82	1.79
<i>Xylene 24 h results</i>						
Amount remaining in solution (mg/g)	0.005	0.030	0.017	0.030	nm*	0.059
Amount sorbed (percent of standard)	97	84	91	84	nm	68
Sorption capacity (mg/g organic carbon)	2.92	3.69	3.00	3.88	nm	3.82
$k_{oc}$	584	123	176	129	nm	64.7
$\log k_{oc}$	2.77	2.09	2.25	2.11	nm	1.81
<i>Toluene 24 h results</i>						
Amount remaining in solution (mg/g)	0.173	0.149	0.167	0.162	nm*	0.132
Amount sorbed (percent of standard)	63	68	65	66	nm	72
Sorption capacity (mg/g organic carbon)	4.83	7.64	5.41	7.70	nm	10.2
$k_{oc}$	27.9	51.3	32.4	47.5	nm	77.6
$\log k_{oc}$	1.44	1.71	1.51	1.68	nm	1.89
<i>Toluene 12 day results</i>						
Amount remaining in solution (mg/g)	0.062	0.098	0.072	nm*	nm*	0.111
Amount sorbed (percent of standard)	87	79	85	nm	nm	76
Sorption capacity (mg/g organic carbon)	6.63	8.87	7.11	nm	nm	10.9
$k_{oc}$	107	90.5	98.7	nm	nm	98.0
$\log k_{oc}$	2.03	1.96	1.99	nm	nm	1.99

\*Peat type not monitored.

**Figure 2.3 Sorption data for six different peat types. Initial concentrations are approximately; benzene = 1780 mg/l, toluene = 470 mg/l and xylene = 185 mg/l (from: Cohen et al., 1991).**

The  $K_d$  value of the different peat types can be determined from figure 2.3 and are shown in table 2.1. The experimental results of Cohen et al. (1991) seem to indicate that even at high aqueous phase concentrations the linear adsorption isotherm could be used to describe the data found. However, it has to be kept in mind, that Cohen et al. (1991) did not have variation in their experiment (initial concentration and mass of peat were kept constant).

**Table 2.1  $K_d$  values for benzene adsorption to peat which are derived from the data of Cohen et al. (1991).**

Material	$f_{oc}$	$K_d$ (l/kg)
okefenokee	0.51	102.77
loxahatchee (Nymphaea)	0.54	49.439
minnesota	0.53	39.664
loxahatchee (sawgrass)	0.54	34.03
Okefenokee (Nymphaea)	0.52	32.068
Maine sphagnum	0.52	31.746

Cohen et al. (1991) found some good correlations between peat characteristics and adsorbency of hydrocarbons. In general, they found that the best hydrocarbon adsorbing peats tended to be low in fibre content, low in birefringent organics, high in ash content, high in guaiacyl lignin pyrolysis products and high in furan pyrolysis products. The birefringence organics give a rough estimation of the amount of non-decomposed cellulosic tissue present in the peat. Novoselova and Sirotkina (2008) mention also the importance of granular size (table 2.2). The best adsorption was observed with smaller particle sizes (0.5-2 mm). In underlying study a natural peat has been used which has been frozen (see chapter 5). When a peat has been frozen, the natural fibre structure breaks, due to which the particle size decreases. So, it is expected that a peat which has been frozen will adsorb more than unfrozen 'natural' peat. This has to do with an increase of specific surface (adsorption capacity).

**Table 2.2 Sorption capacities of various peat fractions (from: Novoselova and sirotkina, 2008).**

Proposed sorbent	Particle size (mm)	Sorption capacity (g/g) for	
		kerosene	diesel fuel
Plant residues	<3	3.21	4.10
Coarse fraction	2-3	4.87	5.52
Medium fraction	1-2	6.08	7.34
Small fraction	0.5-1	6.38	7.35
Coarse dust fraction	0.25-0.5	5.51	6.23
Fine dust fraction	≤0.25	5.26	6.04

Rael et al. (1995) evaluated candidate materials for the removal of benzene. Batch experiments were conducted to construct adsorption isotherms for peat, zeolite, sawdust, coal, 3% PAC (powder-activated carbon)/sand, 10% PAC/sand and GAC (granular-activated carbon). All the batch samples were mixed with an initial benzene concentration of 20 mg/L and various amounts of adsorbent, thereafter the samples were mixed for 72 hour. The fit of the data to the resulting Freundlich equation was good for GAC, fair for the PAC/sand mixtures, and poor for the remaining data (Rael et al., 1995). From the data it was decided to do a column experiment on the 3% PAC/sand mixture. For peat they found the following Freundlich equation parameters;  $K_f = 0.002$  L/g and  $n = 0.56$ . But again, the fit was poor.

The properties of peat depend on several factors, including the ambient conditions existing during its formation, the extent of its decomposition and the method of harvesting. Although, composition is essentially unchanged, other properties of the peat will change significantly when it is removed from its natural state in the bog and is drained, air or mechanically dried, milled, frozen or comminuted. Properties that could undergo a change are; moisture-holding capacity, porosity and

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permeability (Couillard, 1994). These, differences in properties together with the chemical differences described by Cohen et al. (1991) between different kinds of peat make it hard or even impossible to compare results that are found in literature.

### **2.3 Biodegradation**

In contrast to adsorption, which only retards a contaminant for a specific time, biodegradation effectively removes organic contaminants from a soil. Whether biodegradation occurs is however determined by the natural conditions of the soil/groundwater and the contaminant characteristics. The redox condition is most often a determining factor of importance. Especially, the mobile organic contaminants which are persistent in anaerobic soils are often found in plume areas. In underlying thesis a worst case scenario is studied in which only adsorption of these contaminants in the adsorption drain occurs. However, it is quite possible that the persistent contaminants are also easily mineralised in the adsorption material under more oxidized conditions. This could play a role for contaminants such as; benzene, monochlorobenzene, vinyl chloride, MTBE, the light aliphatic fraction of mineral oil, etc (see appendix 5 for degradation rates). Together with oxidation of persistent contaminants in peat, the peat itself will be oxidized as well, which reduces the adsorption capacity.

The interface between groundwater and surface water could play an important role for the degradation of these compounds. This natural attenuation (NA) interface is characterised by more oxidized conditions than the groundwater such that the persistent contaminant could be degraded. The NA-interface is defined by Middeldorp et al. (2003) as the zone of the soil/surface water partition, in which a redox gradient ranges from strongly negative (methanogenic) to positive (aerobic).

Middeldorp et al. (2003) distinguishes two distinct types of interfaces: 1) interfaces with large advective transport, in which oxygen rich water can infiltrate, 2) interfaces with negligible advective transport (steady state), in which oxygen penetration is only determined by dispersion and diffusion. The second interface occurs when there is only upwelling of anaerobic groundwater, such as in the drain. Since, oxygen transport is determined by dispersion and diffusion the penetration is limited to a depth of only a few mm to cm.

Middeldorp et al. (2003) dug a ditch of 30 by 4 m at a monochlorobenzene contaminated site to study an artificial steady state NA-interface. The seepage to the ditch was estimated to range between 20 to 120 mm/day. The data showed a clear anaerobic-aerobic interface in the upper 2-3 cm of the sediment. Oxygen was absent at 2 cm below the sediment surface. Also, the monochlorobenzene measurements showed a sharp decrease towards the sediment surface. It was however concluded that the resolution for monochlorobenzene measurements was not high

enough to tell biodegradation from physical natural attenuation processes (Middeldorp et al., 2003) such as dispersion and diffusion.

Middeldorp et al. (2003) concluded that for the modelled (steady state) pilot the estimated thickness of the interface varied between 1 mm and 1.5 cm for oxygen and nitrate up to 3 cm for non-reacting species. The decrease of the contaminant when approaching the surface water was mainly due to dispersion. Biodegradation could contribute to the decrease of monochlorobenzene concentrations up to 55% under favourable model assumptions. Under advective transport (studied at a tidal influenced site) the thicknesses of the interfaces were approximately 2-6 cm, due to infiltration of surface water. In this case biodegradation can be very large if the pollutant strongly adsorbs to the soil material, due to which the residence time of the plume is relatively large. In that case, the infiltrating oxygen plume and the retarded plume of the pollutant mix strongly, which gives a good condition for biodegradation (Middeldorp et al., 2003).

Penetration depth of oxygen is a crucial factor for the NA-interface and is maximal for sediments with low oxygen consumption, high dispersion and small upwelling (Middeldorp et al., 2009). The oxygen consumption of organic matter is high, because it is also degraded under oxygen rich circumstances. However, adsorption on organic material increases the biodegradation potential because it increases the residence time. Furthermore, the organic material could form a good attachment site for bacteria, which further increases the biodegradation potential.

When the mobile contaminants which are persistent in anaerobic soils eventually enter the surface water they will also be degraded. In this case the residence time in the surface water of the drain (ditch) will determine the effluent concentration of the drain water which is discharged to natural surface waters. When concentrations in the drain locally become too high, because inefficient removal by the organic material and biodegradation, contact risks have to be avoided.

## **2.4 Organic material as a barrier**

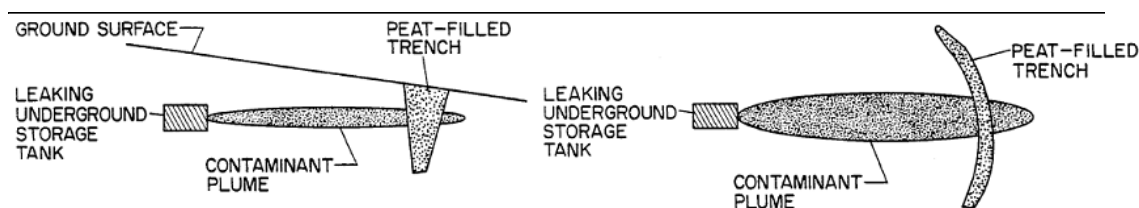
A contaminant barrier is a frequently used in-situ technique to remediate a groundwater contamination. Most of the time barriers consist of air sparging (biodegradation and volatilisation), substrate (biodegradation) or metallic iron (chemical reduction). Adsorption barriers are not common in The Netherlands. The barrier material determines the lifespan and functionality of the remediation system. A barrier which relies on sorption and precipitation of the contaminants, such as peat barriers, are limited in their life span because there is an ultimate capacity of the medium to facilitate appropriate removal reactions. Once the ultimate capacity of the medium is exhausted, contaminant breakthrough will occur. Breakthrough has previously been observed with peat used to remove dissolved and free phase petroleum hydrocarbons from water (McGovern et al., 2002; from: Stehmeier, 1989). On the other hand, the higher the distribution coefficient of a contaminant and the lower the concentration, the longer the life span before

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breakthrough will take place. In some situations, for example pesticides in low concentrations, an adsorption barrier will therefore never break through.

The study of Cohen et al. (1991) is related to the patent of Cohen (1991). In this patent Cohen claims a method for in-situ removal of hydrocarbon contaminants from groundwater with a peat barrier. The results which are found in Cohen et al. (1991) are used to prescribe preferred characteristics of peat that are used in the barrier. The barrier set-up is like a conventional permeable barrier system, in which the barrier is build down gradient from a contaminant plume and the trench depth is below the maximum depth of the contaminant (figure 2.3). Cohen (1991) did however no case study to further investigate applicability of this set-up. There are only few articles about remediation with a permeable barrier system in which peat or organic matter is used as reactive material.



**Figure 2.4 a) Side view of permeable barrier with peat. b) Top view (from: Cohen, 1991).**

A peat barrier system was constructed by McGovern et al. (2002) to remediate groundwater that was contaminated with toluene, ethyl benzene, xylene and n-alkanes in the C<sub>6</sub>-C<sub>36</sub> fraction range. The barrier consisted of an air sparging unit upgradient of a blend of peat materials with a volume of 30 m<sup>3</sup> (with a moisture content of 40%). The removal capacity of peat was based on the article of Cohen et al. (1991), and was assumed to be 20 kg/t peat (dry weight basis). The breakthrough of hydrocarbons was expected after 210 days if 1.1 kg hydrocarbon per day would enter the gate. This estimate was considered to be conservative because they did not take biodegradation into account. After 10 months the removal efficiencies for the gate were determined and varied from 63-96% for the monoaromatic hydrocarbons, 67-81% for the n-alkanes in the C<sub>6</sub>-C<sub>28</sub> fraction range and were lowest (54%) for the C<sub>29</sub>-C<sub>36</sub> n-alkane fraction. The removal efficiencies were enough to reach the regulatory requirements. It has to be kept in mind however, that these removal efficiencies are the combined effect of air sparging and peat sorption.

McGovern et al. (2002) compared their field data with a laboratory study of Kao and Borden (1997) in which removal efficiencies of 86, 71, 43, 28 and 10% for respectively toluene, ethylbenzene, m-xylene, o-xylene and benzene, were reported. Kao and Borden (1997) did a column study to a nutrient briquette-peat barrier system in which denitrifying conditions were established for biodegradation. They found that only 20% of the total BTEX was removed by peat

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due to adsorption and the remaining removed percentage was caused by degradation. From this they concluded that a peat barrier alone would not be efficient for the removal of volatile aromatic hydrocarbons.

Dull et al. (2005) did a case study to a woodchip trench barrier system at the BP Whiting Refinery in Whiting, Indiana. The trench intersects the lube oil contaminated groundwater and is filled with a mixture of woodchips, finely powdered oven dried peat moss and native soils. The trench was designed to restrict the lube oil migration through adsorption onto the peat moss and woodchips, and by aerobic biodegradation by aeration of the trench. Additionally to adsorption, the organic material could behave like a good attachment and nutrient material for micro organisms (good habitat). The aeration of the trench was established by solar-powered blower fans which draw air through horizontal perforated pipes within the trench. Two years of monitoring data showed that the trench prevented the migration of lube oil and that the system worked as an aerobic biodegrading remediation system.



### **3 Capture depth of an interceptor ditch – literature review**

The adsorption drain, a partially penetrating ditch, has to work as an interceptor system to control a contaminant plume. In the 90's research has been done to the effectiveness of this kind of interceptor systems (Zheng et al., 1988; Chambers and Bahr, 1992; Avci et al., 1992). The mechanism of interceptor ditches is essentially the same as that of extraction wells, except that interceptor ditches draw water toward a linear sink, rather than radially. The effectiveness of an interceptor system relies on the establishment of a hydraulic barrier which captures polluted groundwater from upgradient sources in an aquifer, thereby preventing it from moving farther downgradient (Zheng et al., 1988a). The most widespread use of interceptor systems is in aquifers where pollutants are concentrated near the water table such as in cleanup of agricultural chemicals or oil spills. The system is especially favourable above many other remediation systems because interceptor ditches are easily installed and require minimal maintenance. However, effective use of interceptor ditches depends largely on geologic settings and hydrologic conditions. In order to evaluate the effectiveness of a ditch to limit polluted groundwater, it is vital to have a good understanding of the groundwater flow system in the vicinity of the ditch (Zheng et al., 1988a).

Most drainage equations consider the effect of a drainage system on drawdown and distance of influence. Those equations are often based on the Dupuit-Forchheimer assumptions, which assume parallel and horizontal stream lines. Such a flow pattern will only occur when the impervious subsoil is close to the drain (Ritzema, 2006). This assumption does not hold for the interceptor ditch and it is far more important to consider the capture depth of the ditch. Zheng et al. (1988a) developed a numerical and analytical model to calculate the interception depth of partially penetrating ditches. They introduced the concept of the dividing surface (or dividing streamline in a one-dimensional situation) to delineate groundwater flow which is intercepted by partially penetrating ditches (fig. 3.1). An upgradient particle can either discharge into the ditch (intercepted), or travel downgradient beyond the ditch (underflow). If, the depth of the dividing surface or streamline could be calculated, it would be possible to predict whether a contaminant plume will be captured by the ditch. In general, the flow field is complex and three-dimensional in the vicinity of a ditch. However, when the ditch intersects the aquifer fairly straight the problem can be seen as two-dimensional. Zheng et al. (1988a) studied the two-dimensional case, in which the dividing surface becomes a dividing streamline.

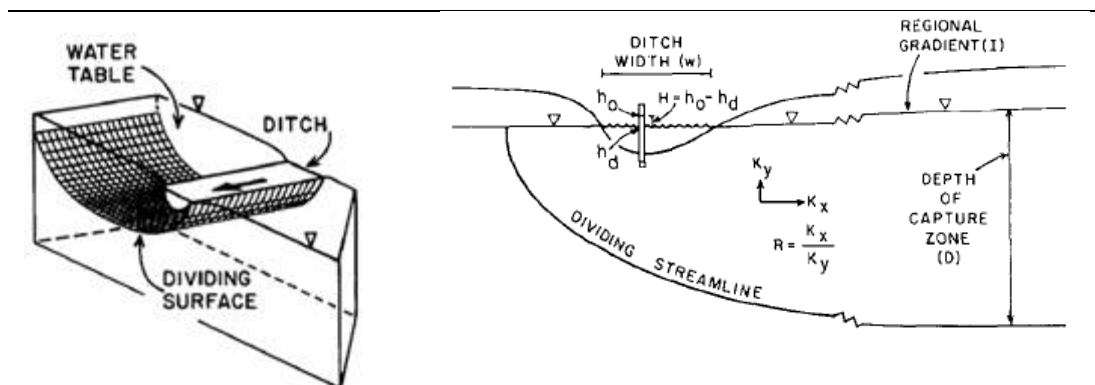


Figure 3.1 The dividing surface (Zeng et al., 1988a) and the dividing streamline (Chambers and Bahr, 1992).

Modeling results presented in Zheng et al. (1988a) indicate that the effective depth of the capture zone,  $D$ , can be estimated by:

$$D = \sqrt{\left(\frac{2wH}{\pi I r}\right)}$$

Where  $w$  is the width of the ditch;  $H$  is the difference between the head in the aquifer and the stage in the ditch ( $h_0 - h_d$ );  $I$  is the (natural) regional gradient; and  $r$  is the ratio of horizontal to vertical hydraulic conductivity (fig. 3.1). The model is based on the following assumptions: the aquifer is infinite in areal extent, infinitely deep, isotropic and homogeneous. The groundwater flow is steady-state and perpendicular to the ditch, and the water table has a uniform gradient (Chambers and Bahr, 1992). Furthermore, to use the equation the assumption that  $lw \ll 2H$  must be satisfied. Because ditches are mostly constructed in shallow aquifers with small water table gradients the equation can also be used if,  $I \leq 0.01-0.001$  and the ditch satisfies  $w \leq 20H$ .

Chambers and Bahr (1992) did a tracer test to evaluate the equation which was found by Zheng et al. (1988a). They injected iodide at two depths and bromide at an intermediate depth in an aquifer which is drained by a partially penetrating ditch. Monitoring wells were used to monitor the flow path of the tracers. The dividing streamline was found on a depth of 3.44 and 4.79 m below the average water table position at a distance of 6.1 m of the ditch. Table 3.1 gives the parameters values for the field site. Using the average parameters for the field site and an anisotropy ratio of 3, the equation predicts that the capture depth during the tracer test would be 3.93 m. Using the extremes of the ranges of estimated parameters for the field site during the test, capture depths range from 1.44 m to 8.05 m. The precision and accuracy of depths predicted using the equation are limited by parameter variability, uncertainty in parameter estimates, and

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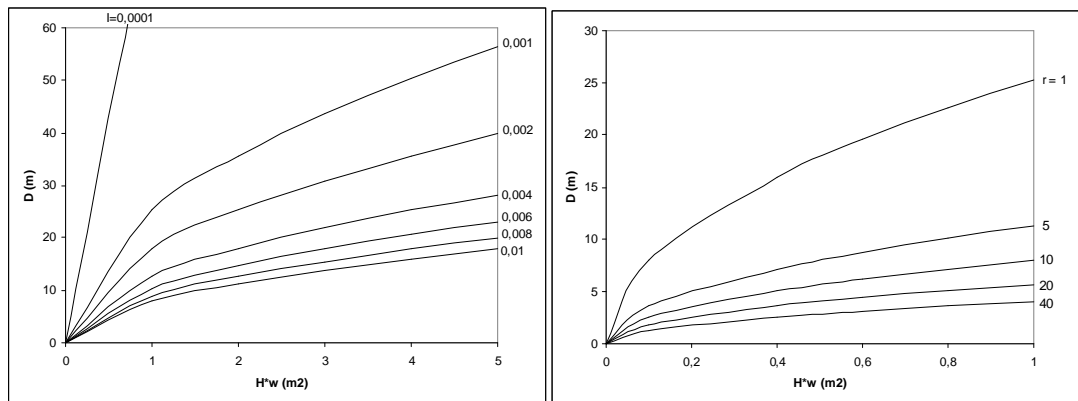
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model assumptions. The range in predicted capture depths from the field site during the tracer test reflects the sensitivity of the equation to each parameter (Chambers and Bahr, 1992). Parameters H, w and l are influenced by environmental conditions due to which they have a temporal variability. The anisotropy ratio, in contrast to the other three parameters, is unlikely to change over time at a given location. However, the ranges of values arise from estimation uncertainty. Chambers and Bahr (1992) conclude that it may not be realistic to expect to obtain precise predictions of capture depth using the simple model of Zheng et al. (1988a), but it is possible to use the equation to estimate the minimum capture depth for a ditch.

**Table 3.1 Parameter values used in the equation to estimate capture depths. The parameters correspondent to values found at the field site (Chambers and Bahr, 1992).**

	Range	Mean value
w (in m)	2.29-3.05	2.95
H (in m)	0.02-0.05	0.037
l	0.001-0.002	0.0015
r	1.5-7	

Figure 3.2 depicts two graphs in which the capture depth is plotted versus the head gradient in the ditch times the ditch width. The anisotropy ratio is kept constant in the left graph and varies in the right where the gradient is the constant. These figures (based on Zheng et al. (1988a)) graphically show the effect of H, w, l and r on the capture depth and can therefore be used for the design or evaluation of interceptor ditches.

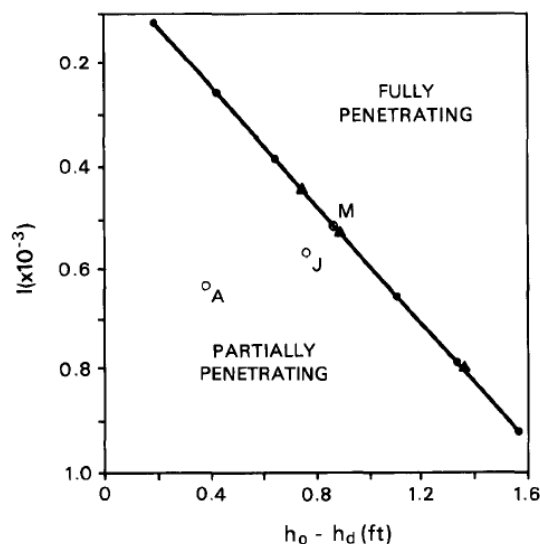


**Figure 3.2 Relationship between the capture depth and the product of H (head in the ditch minus the head in the aquifer) and w (ditch width). In the left figure the anisotropy ratio (R) is assumed to be 1 and each line represents a particular value of I. In the right figure the regional gradient (I) is assumed to be 0.001 and each line represents a particular value of r. The figure is based on Zheng et al. (1988a).**

Zheng et al. (1988b) studied the effect of seasonal variation and hydrological conditions on the effectiveness of an interceptor ditch, located in a portion of the Central Sand Plain of Wisconsin. Field data of May, July and August were used to calibrate and evaluate the model. Data collected in May was used as initial situation when the ditch was fully penetrating. In July the ditch stage lowered and the regional gradient increased, which led to a partially penetrating capture depth. However, in contrast to August the capture depth was still almost fully penetrating. In August both the ditch stage and the regional gradient increased, which led to a shallow capture depth. This result is in agreement with the capture depth equation, ditch stage and water-table gradient are inversely proportional to the capture depth. The effect of hydrological conditions, including the regional water-table gradient, the recharge/ discharge distribution and the ditch stage, on the effectiveness of the interceptor ditch can be described by two parameters I and  $h_0-h_d$ . Model simulations indicated that when the recharge/ discharge distribution changes,  $h_0-h_d$  will change with approximately the same amount. These parameters provide an easy way to evaluate the effectiveness of the ditch because I and  $h_0-h_d$  can simply be measured in the field (Zheng et al., 1988b). Figure 3.3 was constructed by Zheng et al. (1988b) by varying I and  $h_0-h_d$  for situations where the dividing streamline was fully penetrating. This figure can be used to estimate, whether a ditch has a fully penetrating capture depth based upon measured I and  $h_0-h_d$ . The graph also shows the field data of May, July and August; the further the distance to the left of the line, the more underflow occurs, or the less effective is the interceptor ditch.

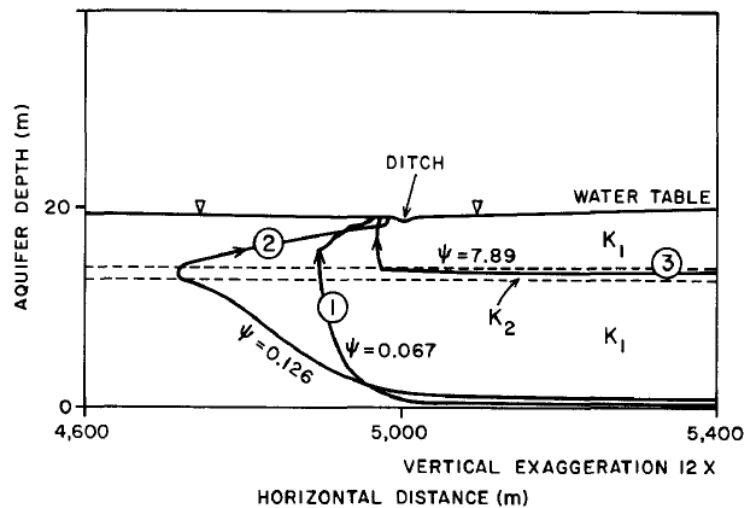
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**Figure 3.3 effects of hydrological conditions on the effectiveness of interceptor ditches. The circles, labelled M, J, and A, represent simulations of May, July and August. Solid dots indicate simulations in which recharge/discharge distribution for May was used, and the triangular points in which that for August was used (from: Zheng et al., 1988b) (1 ft = 0.3048 m).**

Zeng et al. (1988a), also constructed a numerical model in which the effect of variation in hydraulic conductivity was evaluated. Three cases were compared, in which all parameters except the conductivity were the same. Figure 3.4 shows the results of the three cases; interceptor ditch in a homogeneous aquifer (case 1), in an aquifer with a low-conductivity layer (case 2) and an aquifer with a high-conductivity layer (case 3). The results indicate that the dividing streamline extends down gradient in an aquifer with a low-conductivity layer compared to a homogeneous aquifer. There is however limited effect on the depth of the dividing streamline. The depth of the dividing streamline is strongly controlled, when there is a high-conductivity layer present in the aquifer. Most flow through the cross section is transmitted within this high-conductivity layer and therefore the dividing streamline is affected by that.



**Figure 3.4** Effect of aquifer heterogeneity on the dividing streamline. In case 1 the aquifer is homogeneous ( $K_1=K_2$ ) but anisotropic. In case 2 the  $K_2$  is 100 times smaller than  $K_1$  and in case 3  $K_2$  is 100 times greater than  $K_1$ . The dimension of  $\psi$  is  $m^2d^{-1}$  (from: Zheng et al. 1988a).

In general it can be stated that the interception depth of a partially penetrating drain is largely depending on the local hydrological characteristics of the aquifer and drain. The hydraulic gradient between aquifer and drain determines the discharge into the drain. Precipitation will influence this gradient seasonally.

A 2D model has been build in MODFLOW (paragraph 6.1.2), because of the high sensitivity of the formula given by Zheng et al (1988a). The content of paragraph 6.1.2 is based on the results of Zheng et al. (1988a), but model parameters are based on parameters found at a Dutch landfill site (Kanaalpolder). This chapter and paragraph 6.1.2 can be used to make an estimation of the necessary drain parameters to establish a hydraulic barrier. Paragraph 6.1.2 simplifies the interpretation for application in the field, because results are given versus discharge into the drain, instead of hydraulic gradient, such as been done by Zheng et al. (1988a).

## 4 Materials and methods

As part of this MSc research, hydraulic conductivity and adsorption (batch and column) experiments have been done on five different processed peats and a green-compost. The peat-materials are supplied by the firm Intervema bv, Griendtsveen AG, a peatery in Edewecht (Germany). The green-compost is supplied by Delta Milieu, a composting company in Nieuwdorp (Zeeland, Netherlands).

The experiments have been conducted partially in Deventer (Tauw bv) and partially in Utrecht (University of Utrecht). The water sample analyses are outsourced to AL-west, which is a NEN-EN-ISO/IEC 17025 accredited laboratory, situated in Deventer.

An additional reason for the experiments was the planned remediation of a landfill with chemical waste on a sandy soil near Philippine (Zeeland, The Netherlands). The experiments have to indicate the added value of organic material in a drainage trench, which is planned to be constructed at this location. Due to the sandy subsoil a leachate plume has develop with volatile chlorinated and non chlorinated hydrocarbons. A remediation concept, in which a draining circular ditch is used (fig. 4.1), was described in the report with remediation possibilities for this site (Praamstra and Van der Ham, 2009). Field experiments are done at the location with Peat 05 and Green compost. When the results are available the data should be compared with results found in this thesis.

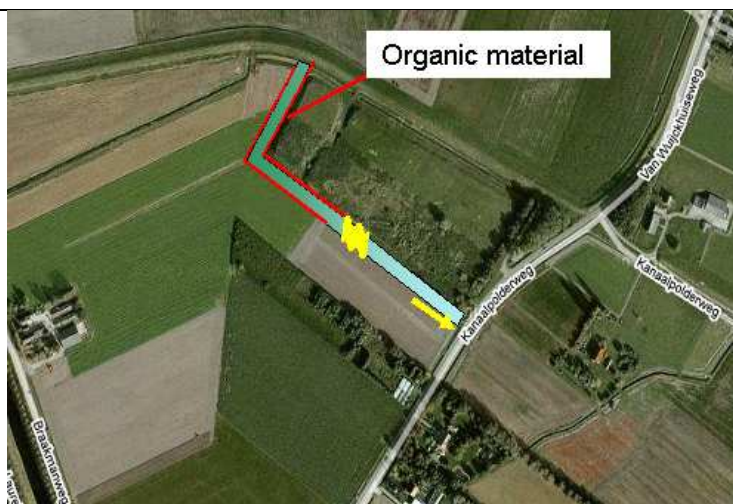


Figure 4.1 Drawing of a possible risk reducing remediation variant at Kanaalpolder.

Not all supplied materials were suitable for the hydraulic conductivity experiments. Therefore, from a visual selection, the following materials were chosen to be tested (fig. 4.2):

- 01: Best quality, frozen, mature peat
- 02: peat fibre
- 05: sieved/milled product of dried white peat turf
- 10: finest fraction of 01, after drying (residual moisture 5%)
- 11: aquaria purification, DTG-A
- Green-compost (sieved on 20 mm (on 11.2 mm for benzene tests and column experiment)).

Furthermore, in previous experiments by Tauw bv, two natural undisturbed peat samples have been tested. The results of these experiments will also be shown in this thesis. Figure 4.3 shows the method of sampling and the alignment in the columns.

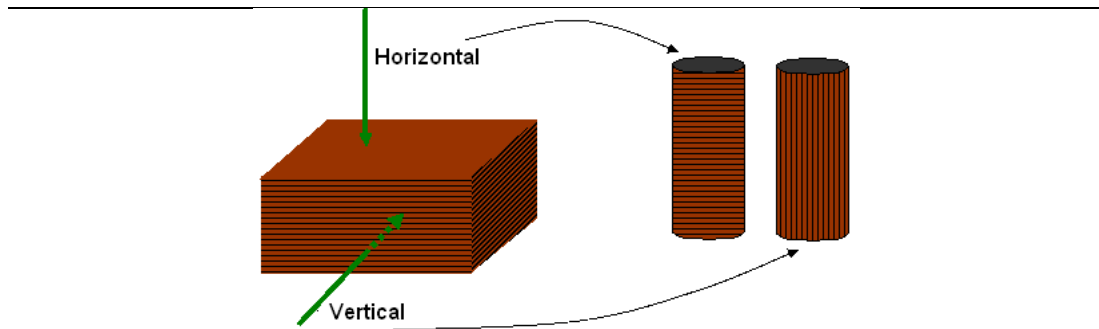
- Undisturbed black peat, horizontal
- Undisturbed black peat, vertical



**Figure 4.2** The adsorption materials: 01) crumbly, fine material which is used as garden soil. 02) hairy, fibre like material. 05) fine to coarse material, richer in fibre content than 01. 10) very fine dusty material. 11) grain structure with a diameter of approximately 5 mm (used in aquaria). Green compost) Green compost with coarser parts from twigs and such.

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**Figure 4.3 Method of sampling of undisturbed peat and alignment in column.**

#### 4.1 Hydraulic conductivity experiments

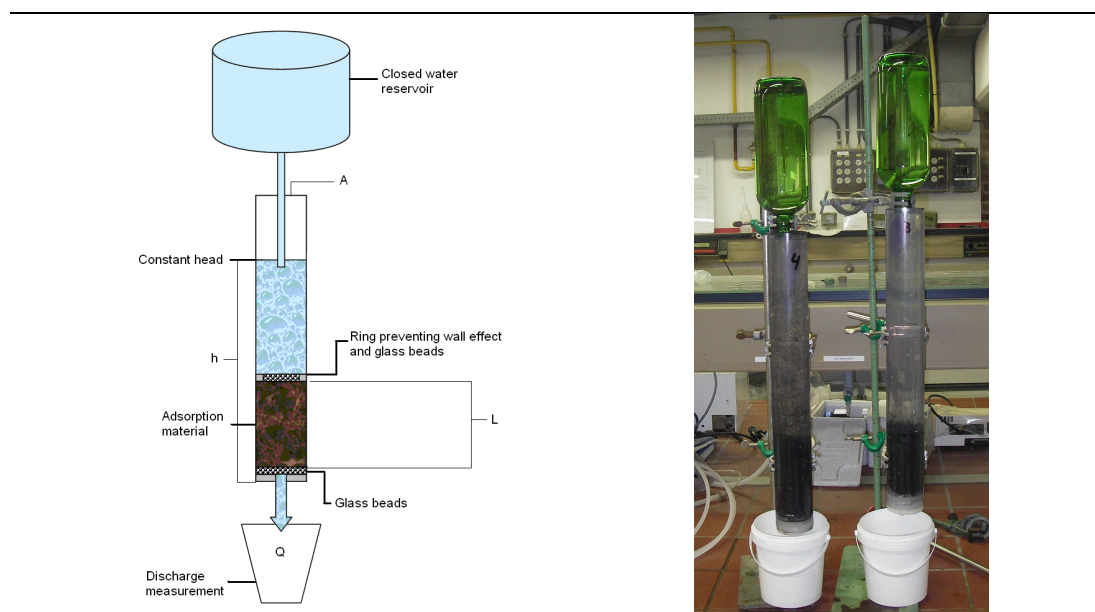
The hydraulic conductivity is measured with the so called 'constant-head test'. During this procedure water moves through the soil under a steady state head condition while the discharge of water flowing through the soil specimen is measured. Figure 4.4 shows the setup of the experiment. The closed water reservoir on top ensures that the water-column on top of the soil specimen is kept constant. By knowing the discharge of the water ( $Q$ ), the length of the soil specimen ( $L$ ), the cross-sectional area of the specimen ( $A$ ), and head ( $h$ ), the hydraulic conductivity ( $K$ ) can be calculated using Darcy's law.

$$Q = A \cdot K \cdot i, \quad \text{with } i = \frac{h}{L}$$

$$K = Q / (A \cdot i)$$

Hydraulic conductivity tests are done to get insight in the hydrological characteristics of the potential adsorption-materials. The conductivity is very important for the construction of the adsorption drain, because it determines the head gradient which has to be reached between the groundwater and the water in the drain. The ratio between the soil conductivity and adsorption-material conductivity has to be as low as possible, such that there is a low resistance for the groundwater to enter the drain.

Due to the construction of the test with a 1 litre bottle as closed reservoir (fig. 4.4) it was necessary to carry out the experiment over 2 days in 2 phases. The test was stopped during the night and continued the next morning, because the water could not be replenished. This was not a problem in the previous test, for undisturbed peat, because these conductivities were much lower than the materials tested during this experiment.



**Figure 4.4 Schematic drawing and picture of the setup of the constant head test.**

A column with an inside diameter of 5.2 cm is used. In every column a layer of adsorption material (L) with a thickness of 8.5 to 11 cm is fitted and lightly pressed. Thereafter, the material is wetted and a water column of 32.5 to 36 cm is put on top of it (appendix 1).

## 4.2 Batch adsorption experiments

The adsorption effectiveness or capacity of a substance in a common solute can be determined by adsorption isotherms that describe the adsorption capacity of a selected adsorbent (Rael et al., 1995). The adsorption isotherm can be determined by batch static-equilibrium adsorption studies. Roy et al. (1992) describes two experimental techniques which are used to generate batch adsorption data:

1. The constant solid:liquid ratio method: mixing a batch of aqueous solutions, each solution containing progressively decreasing solute concentrations, with adsorbent. The amount (by weight) of adsorbent is kept constant in all solutions.
2. The variable soil:solution ratio method: mixing a batch of solutions, all containing the same solute concentration, with progressively increasing amounts of adsorbent.

In both cases the measurements are taken when the system has equilibrated. Roy et al. (1992) suggests that the equilibrium time should be the minimum amount of time needed to establish a

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rate of change of the solute concentration in solution equal to or less than 5% per 24 hr interval. From Cohen et al. (1991) it is concluded that an experimental runtime of 24 hr should be enough to reach equilibrium sorption of benzene to peat.

Two batch adsorption experiments have been done for this study, both at room temperature ( $\pm 20^{\circ}\text{C}$ ). In the first experiments all materials, with the exception of material 02, have been tested on adsorption capacity. For these experiments liquid:solid (L/S) ratio's of approximately 20 and 50 have been made. The liquid came from a landfill leachate from which water samples were taken at 7 August 2009. The groundwater at the sampling location (Philippine, Zeeland, The Netherlands) is contaminated with aromatics, chlorinated hydrocarbons and chlorobenzene. The professional laboratory AL-west analyzed one bottle of the groundwater samples (table 4.1) and the remaining samples were made abiotic and stored without head-space in a refrigerator at  $7^{\circ}\text{C}$ . Thereafter, these samples were used in the adsorption experiments which were conducted on 12 October 2009. A blanco was used to measure losses during the experiment, which have nothing to do with adsorption (such as volatilization). The adsorption experiments on undisturbed peat were conducted previously with another leachate of the same location. Only the results of these experiments will be discussed in this thesis.

**Table 4.1 Concentration of the contaminants in the initial groundwater sample taken from a landfill leachate at 7 August 2009. This sample was stored before it was used in the batch experiments.**

Contaminant	Initial leachate sample (µg/l)
Benzene	140
Toluene	58
Ethyl benzene	2500
Xylenes	110
C10-C40	400
C10-C16	230
C16-C22	170
1,2 dichlorobenzene	<d (smaller than detection limit)
1,4 dichlorobenzene	<d
Mono-chlorobenzene	94
Naphthalene	10
Chloroethane	3000

After the first experiments, the adsorption capacity of peat 05 and green-compost are further investigated with a 'self-made' benzene solution. A stock saturated benzene solution was prepared by adding an excess (500 µl) of pure (99.7%) benzene to 50 ml of MQ water, shaking vigorously, and allowing the two phases to separate and equilibrate. In order to maintain saturation and to prevent volatilization, the separate phase was allowed to 'float' on top of the saturated water solution. 2.5 ml of the stock solution was injected in 2250 ml demi water such that a solution with a concentration of approximately 2 mg/l was expected (equal to concentrations that were found in the field near the landfill and high enough for significance during analyses). The blanco batch showed the obtained concentration, because the exact concentration of the stock solution is not known, but presumed to be equal to its solubility in water (1780 mg/l). Also, the blanco is used to make sure that losses during the experiment are taken into account.

Dry weight and moisture content is determined using a *Sarorius MA 30 – moisture analyser* at 105°C. This was redone for peat 05 and green-compost because new samples were used during the benzene adsorption tests. For this test the green-compost was sieved on an 11.2 mm sieve. Besides that, to see the effect of sample size, a larger sample was oven-dried using a carbolite furnace at 105°C for 24 hr.

The materials were put into glass vials in the original moist state, because drying of the materials could influence the adsorption capacities. Studies of the effect of moisture content of peat on its

sorption properties have shown that a decrease in the moisture content changed the adsorption capacity for oil (Novoselova (2008), see also paragraph 2.2). Furthermore, it was the intention to exclude headspace, but this has not always been possible. Therefore, losses due to volatilization have to be taken into account when the results are interpreted.

The adsorption is calculated from the data, with the following formula:

$$S_{eq} = \frac{V_w C_0 - (V_w + V_m) C_e}{M_s}$$

In which  $S_{eq}$  is the mass of adsorbed solute per mass of dry soil,  $C_0$  is the initial concentration,  $C_e$  is the remaining (equilibrium) concentration in the effluent (filtrate),  $V_w$  is the added solution volume,  $V_m$  is the moisture content of the material and  $M_s$  is the mass of dry soil.

## 4.3 Column experiments

### 4.3.1 Column characteristics and tracer experiment

The experiments were performed in three columns made of glass. The columns were 50 cm long and 4.5 cm in (inner) diameter. Top and bottom lids were stainless steel, with an inlet in the middle for the liquid flow. Between the lid and the soil, a glass porous plate was placed to spread the liquid equally over the porous medium. The stainless steel lids were made water tight by a viton o-ring that was placed between the lid and a ring around the column and secured with bolts. The top and bottom lids were connected to each other by three rods (similar to: Langevoort, 2009). Two columns were filled with organic material (peat 05 and green compost) and one column was filled with sand (Quartz sand H31, Sibelco, Belgium). The sand column was used as reference column and had grain diameters between 0.1 and 1 mm with a median diameter of 0.4 mm. The sand column enclosed air due to settling of the sand, this resulted in approximately 1 cm of unfilled column. During transport of the column the air was encapsulated by the sand which resulted in a no-flow area. Although this was not desirable, it is also not a real problem, because these situations also occur in the ground (fig. 4.6).

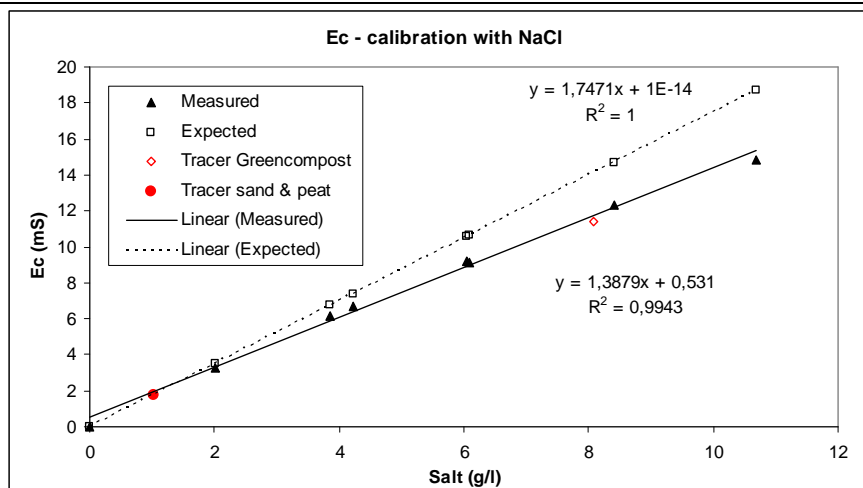
The columns are weighted before they were filled with material, when they were filled with material and after the material was saturated with demi water. The characteristics of the filled columns could be determined from this data (see table 4.2). The columns were saturated by pumping the demi water with a peristaltic pump (Meyvis – minipuls 3) from the bottom into the columns. The pump was calibrated by measuring the time it takes to pump 1 ml at 10% of the maximum pump velocity. This was done until 10 ml was pumped, such that the average velocity could be calculated. At 10% of the maximum pump velocity (4.8) the discharge was 12.22 ml/hr.

For the experiments a pump velocity of 3.2 was used, which thus approximately equals a discharge of 8.15 ml/h. This was later verified by measurements of discharge out of the columns.

**Table 4.2 Characteristics of the column. The empty weight of the peat column is the average of the two columns, because the column was already filled before it was weighted.**

Material	Volume (cm <sup>3</sup> )	Empty (g)	Full (g)	Saturated (g)	Matter (kg dm.)	Water (ml)	Bulk density (g/cm <sup>3</sup> )	Porosity (-)
Peat	795.2	1507.5	1706.9	2237.7	74.62	655.58	0.094	0.82
Green compost	795.2	1504.0	1971.6	2416.9	280.42	632.48	0.353	0.80
Sand	795.2	1511.0	2768.0	3063.3	1257.00	295.30	1.581	0.37

The column was flushed with demi water for 6 hours after which electrical conductivity was measured. The electrical conductivity was measured with a 'Knick'-digital conductor measurer, which was calibrated with a 1 M KCl-solution, with a conductivity of 102.1 mS at 20 °C. Thereafter, several NaCl-solutions were made with known concentrations from which conductivity was measured. Figure 4.5 gives a comparison between the measured conductivity and the conductivity which is expected from the amount of NaCl that is added and the calibration with KCl. Furthermore, it depicts the characteristics of the two prepared tracer solutions.



**Figure 4.5 calibration of the electrical conductivity measurer.**

The conductivity measurer is cleaned with demi water after every measurement, such that the measurement thereafter is not influenced by the previous. The conductivity measurer is also flushed several times with the sample, before the value is noted. This is done to prevent dilution

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due to the demi water, which was used for cleaning. A salt solution was prepared with concentrations that were based on the found 'initial' electrical conductivities of the columns. Table 4.3 gives an overview of the initial electrical conductivities and the prepared salt solutions. Both conductivities are measured several times such that a standard deviation could be given.

**Table 4.3 Initial electrical conductivities of the columns and the electrical conductivity of the salt tracer. Initial conductivity of green compost effluent was high, therefore the tracer conductivity had to be high as well, such that the difference could be easily measured.**

Column	Initial conductivity (mS)	Tracer conductivity (mS)
Green compost	5.80 ( $\pm 0.035$ )	11.39 ( $\pm 0.57$ )
Peat	0.038 ( $\pm 0.0017$ )	1.78 ( $\pm 0.055$ )
Sand	0.015 ( $\pm 0.0011$ )	1.78 ( $\pm 0.055$ )

The salt solution was pumped in the columns with a rate of approximately 8.15 ml/hr for 90 hours, after that demi water was injected again. The outflow was measured on conductivity several times during and after the injection of the salt solution.

#### 4.3.2 Column benzene adsorption experiments

Biodegradation of benzene is fast in aerobic environments and slow in anaerobic environments. In the field situation, the plume will most likely be anaerobic and therefore biodegradation will be slow. To represent the average field situation in The Netherlands as close as possible it is chosen to make the columns abiotic, such that no biodegradation will occur. This situation will represent a worst case scenario for the field case, because the peat will only retard the pollutant. It is however important to know what the retardation will be, because this directly influences the residence time in the peat and therefore the potential for biodegradation. Furthermore, it gives an indication of the lifespan of the organic material in the ditch.

It is quite difficult to ensure that the columns are completely abiotic. For this experiment a few methods for sterilisation were reviewed; boiling, adding a toxic (e.g. mercury chloride, sodiumazide) and radiating (e.g. UV, gamma). It was chosen to use gamma-radiation for the sterilisation of the columns and sodiumazide ( $\text{NaN}_3$ ) in combination with boiling for the inlet fluid. The sodiumazide could also be used for sterilization of the material in the column, but it is questionable if all the bacteria will get in contact with the toxic. Gamma-radiation will however also not make the column completely sterile, but in combination with the sodiumazide the remaining bacteria can most likely be neglected.

The gamma-radiation was done by Isotron bv (Etten Leur, The Netherlands), which is a company that especially treats products from the medical, cosmetic, pharmaceutical and food industry.

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They irradiate the products to break the DNA-chains of micro-organisms and stop cell division. Sterile is as they say an absolute term, but the assurance that any given item is sterile is a probability function. Isotron bv works with the 'sterility assurance level (SAL)', which is an European standard and is defined as the probability of any given unit being non-sterile after exposure to a validated sterilization process. For a product to be CE marked and labelled sterile, it needs to conform to the European Standard EN 556. The SAL defined by EN 556 is  $10^{-6}$ , which is one surviving microorganism per one million products. The Standard that defines methods of verifying a given SAL for irradiated products is ISO 11137-2-2006. Isotron bv guarantees that the SAL is reached, when a product is irradiated by a minimum of 25 kGy. This was therefore the requested dose for the columns, which were irradiated by a minimum of 35.3 and a maximum of 43.8 kGy. Irradiation took place with approximately 1 kGy per 10 minutes during approximately 7 hours.



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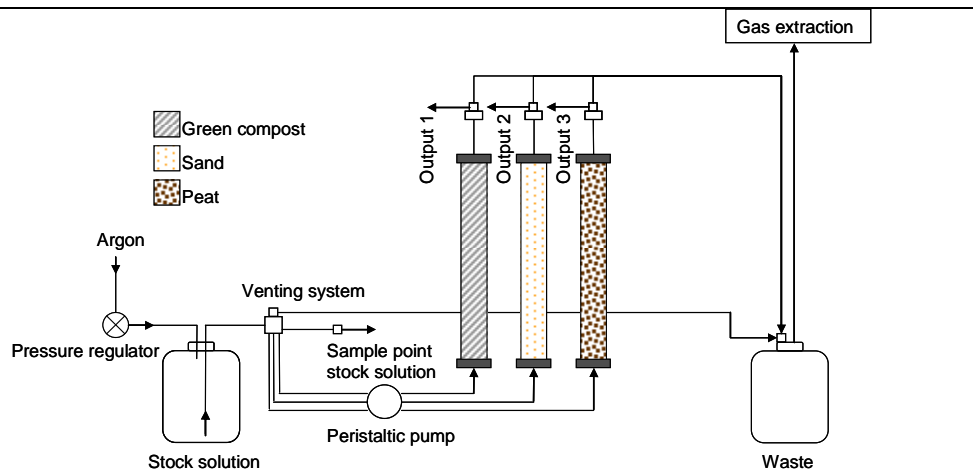
Figure 4.6 Picture of the column experiment set-up and the enclosed air in the sand column.

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**Figure 4.7 schematic drawing of the column experiment set-up.**

Figure 4.6 shows a photo of the experiment set-up and figure 4.7 shows the schematic drawing of the set-up. The stock solution is prepared by adding 0.5 g/l  $\text{NaN}_3$  (after; Rasmussen et al., 2002) to boiled demi water, after the water was cooled down to room temperature. Approximately 2.5 ml of the saturated benzene solution (prepared for batch experiments) was then added to 2 litre of the demi-water to reach a concentration around 2 mg/l. The 2 litre stock solution reservoir is enough for approximately 3 days and has to be changed after that. The reached concentration in the stock solution has to be determined in the laboratory. The concentration of the stock solution will therefore be measured at the start of injection and several times during the injection. In this way losses in the stock solution during the experiment can be determined and the differences between the stock solutions can be compared. The stock solution was put under 0.15 bar argon overpressure to minimize volatilization and to keep pressure on the pump.

If no samples are taken, the effluents of the three columns flow to a waste reservoir. The flow direction can be changed by a valve, when a sample has to be taken. In this way flow of the column is not disrupted and samples are taken at the flow rate of the column. The effluent tube for sampling is a viton tube which is connected to a needle. To prevent pressure build up in the 1.5 ml sampling vial, a special assembly of vials and capillaries was used (figure 4.8; similar to Langevoort, 2009). The headspace of the first vial, containing the sample, was connected to the headspace of a second 1.5 ml vial via a capillary. This second vial was filled with demi water leaving no headspace. This water was connected by another capillary to a third 1.5 ml vial, empty at the start. As the first vial filled up, its headspace pressure increased causing a pressure build up in the second vial, which in turn forced water into the third vial which was open to the atmosphere. Without this setup pressure in the sampling vial could have increased and thus prevented flow of water out of the column into the first

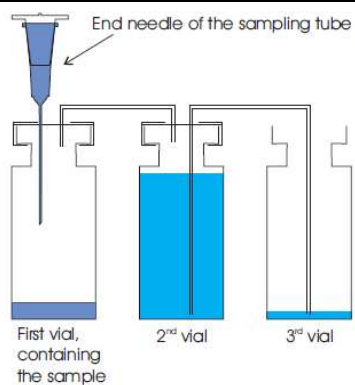
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vial. The assembly allows for keeping the pressure in the vial low and at the same time, minimize the loss of volatile components (Langevoort, 2009).

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**Figure 4.8 Set of 1.5 ml vials and capillaries used to sample with a minimum loss of volatile components (Langevoort, 2009).**

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Recommendations for future column experiments can be found in appendix 5. The recommendations are based on limitations encountered during these experiments.

## 5 Results of the experiments

### 5.1 Hydraulic conductivity experiments

The hydraulic conductivity is determined with the constant-head test; table 5.1 shows the results of the experiments and appendix 1 shows the calculations.

The conductivity (K) of peat 11 could not be determined (table 5.1). This has to do with the coarse grain structure of that material (fig. 4.2), due to which the conductivity was too high to determine with the experimental set-up. The supplier of this pressed peat material informed Tauw about previous research in which the preservation of the grain structure was proven for at least five years. The conductivity will however be affected when it is applied in the adsorption drain due to clogging of the pores by fine material. The extent of the clogging and if counter measures have to be taken has to be determined in the field if applied.

**Table 5.1 Set-up and outcome of conductivity experiments**

Material	Length specimen (cm)	head (cm)	gradient (cm/cm)	K-total (m/d)	K-2 <sup>nd</sup> part (m/d)	%-difference w.r.t. total
Peat horizontal	11	32.5	3.95	0.0193	-	-
Peat vertical	8.5	36	5.24	0.0223	-	-
01	11.5	34.5	4	0.7088	0.2644	-62.69
02	10.5	35.2	4.35	0.8054	0.4224	-47.55
10	9.3	35.4	4.80	0.9096	0.7428	-18.33
05	9.5	35	4.68	1.8923	1.3801	-27.07
Green compost	10	36	4.6	0.4984	0.4811	-3.47
11	10.8	34 - 0	-	-	-	-

Two values of the conductivity and the difference between these values are shown in table 5.1. The second conductivity (K-2<sup>nd</sup> part) is the conductivity which is determined during the second part of the experiment (red circles in figure 5.1 indicate start (left) and end (right) of second part). The second conductivity is determined for peat 01, 02, 10, 05 and green compost after the test was stopped during the night and continued at the second day. From this it becomes clear that the conductivity decreases significantly, due to an increase in wetting time. This can be explained by the characteristics of the material, which swells due to wetting, due to which conductivity decreases.

The static conductivity is determined by the calculation (appendix 1) of the change of conductivity in time, and is approximately equal to K-2<sup>nd</sup> part. The difference between K-2<sup>nd</sup> part and the static conductivity is that K-2<sup>nd</sup> part is calculated as an average of the points found between the red circles and the static conductivity is the value at which the line is stabilized. Figure 5.1 shows the resulting chart from which conductivities are determined; the values are presented in table 5.2.

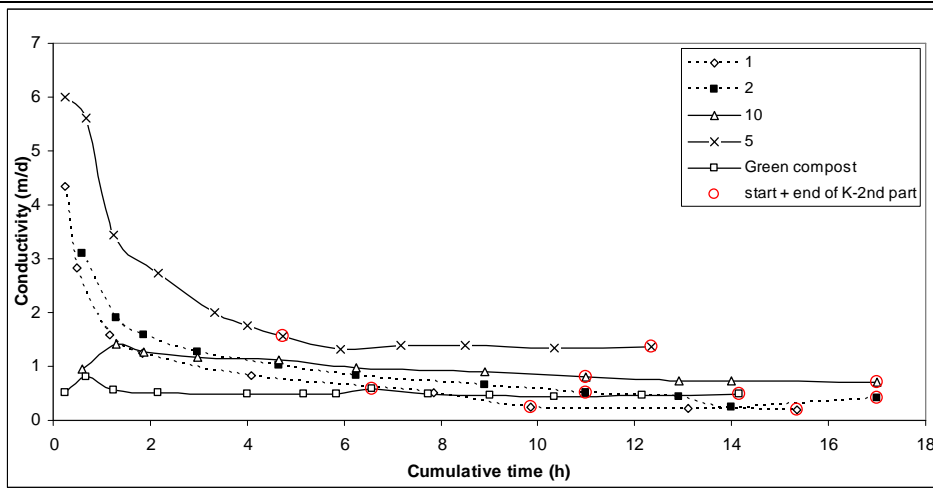


Figure 5.1 Chart with the change of conductivity in time.

Table 5.2 The static conductivity

Material	K-static (m/d)
Peat horizontal	0.019
Peat vertical	0.022
01	0.19
02	0.41
10	0.7
05	1.35
Green compost	0.46

Peat 05 has the highest conductivity (table 5.2). Therefore, this material has the highest potential for use in a draining adsorption ditch (the adsorption drain). Peat 10 has also a high conductivity, but the usability of this material is limited by its structure. The material is very fine which could lead to rapid erosion of the adsorption layer, or clogging of the underlying coarser material. To

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prevent this, a countermeasure should be taken, for example packing of the material in a filter cloth.

## 5.2 Batch adsorption experiments – Part 1

Material 02 was not tested because of the fibrous structure and the relatively small surface area compared to the other materials. Due to that, the adsorption capacity is expected to be (much) lower than for the other materials and is therefore not measured.

During the previous batch experiments on undisturbed peat an average adsorption percentage of 92.9% for L/S = 17.4 and 55.8% for L/S = 65.4 was found (appendix 2). A  $K_d$  value of 170 l/kg was calculated for the data of undisturbed peat.

Table 5.3 presents the characteristics of the batches which were made, with the resulting L/S ratios. It was not possible to get L/S ratios of exactly 20 and 50, due to the fact that the tested material occupies an on forehand unknown volume in the bottle. Furthermore, the ‘wet’ material was used in the test which causes some dilution of the leachate. This dilution is taken into account in the calculation of the adsorption capacities.

**Table 5.3 Setup of the experiments with values for; Percentage dry weight, input wet and input dry material, volume of used leachate, dilution due to moisture content of the material and resulting L/S ratios. (The percentage dry material is determined with a *Sarorius MA 30 – moisture analyser* at 105 °C).**

Organic material	Dry material (%)	Input wet (g)	Input dry (g)	Leachate (ml)	Dilution	L/S ratio
01	26.4	94.7	25.001	437	1.159	20.267
01	26.4	37.9	10.006	493	1.057	52.060
10	84.6	29.6	25.042	411	1.011	16.595
10	84.6	11.8	9.983	479	1.004	48.166
05	48.4	51.6	24.974	394	1.068	16.842
05	48.4	20.7	10.019	475	1.022	48.477
11	70.8	35.3	24.992	483	1.021	19.738
11	70.8	14.1	9.983	511	1.008	51.600
Green compost (20 mm)	74.8	33.4	24.983	498	1.017	20.270
Green compost (20 mm)	74.8	13.4	10.023	518	1.007	52.017
Blanco	-	-	-	534	-	-

The concentrations measured in the batches, are compared to the concentrations which were measured in the blanco. Doing this, the percentage adsorbed for every individual contaminant can be determined. The data (appendix 2) showed however some impossibilities, which could be a result of storage or faults during experimentation. This becomes clear when the concentrations

which are measured on 7 August (initial leachate sample) are compared to the concentrations found in the blanco (table 5.4); almost all concentrations show a large decrease. Furthermore, some concentrations (appendix 2) are lower in the blanco than in the batches. This means that the concentrations in the stored samples deviated from each other, due to which the initial concentrations of the batches were different. This implies that the concentrations of the blanco can not be used to determine the adsorption, because for this it is assumed that losses in the blanco are equal to those in the batches. It is therefore a necessity that the initial concentrations are equal to each other.

**Table 5.4 Comparison of the concentrations found in the blanco and the initial leachate sample. The initial leachate sample is sampled on 7 august 2009 at the landfill Kanaalpolder near Philippine. This leachate is stored and used again for the experiments on 12 oktober 2009.**

Contaminant	Blanco (µg/l)	Initial leachate sample (µg/l)
Benzene	68	140
Toluene	25	58
Ethylbenzene	980	2500
Xylenes	54	110
C10-C40	120	400
C10-C12	55	Not analysed
C12-C16	33	230 (C10-C16)
C10-C16	88	230 (C10-C16)
C16-C20	11	170 (C16-C22)
C20-C24	13	Not analysed
C24-C28	6	Not analysed
C28-C32	0	Not analysed
C32-C36	0	Not analysed
1,2 dichlorobenzene	1.6	<d (smaller than detection limit)
1,4 dichlorobenzene	2.2	<d
Mono-chlorobenzene	50	94
Naphthalene	5.8	10
Chloroethane	2400	3000

The batch concentrations are also related to the initial leachate concentrations (see table 5.5), to at least gain some insight in the adsorption capacities of the materials. From table 5.4 it becomes clear that this results in loss of data, because the initial leachate is not analysed on the same chemicals as the blanco and the batches. This difference has to be kept in mind when the

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average adsorption percentages are compared. Furthermore, the concentration chloroethane is not determined in the batches with peat 11 and green compost.

Table 5.5 shows three different total average adsorptions; 1) total related to blanco, 2) total related to blanco excluding values which are not realistic for this test, and 3) total related to the initial leachate sample. In addition, the adsorption of the individual chemicals are determined, results are shown in appendix 2.

The sentences 'not realistic for this test' in total 2, needs some explanation. As already mentioned some concentrations in the batches were higher than the concentration found in the blanco. When these concentrations are taken into account, it results in a lower total adsorption capacity and for the individual chemicals in a negative adsorption percentage (desorption). This is of course not caused by desorption, but a result of deviating initial concentrations.

**Table 5.5 Average percentage adsorbed at the material, with; Total 1 = total related to blanco, Total 2 = total related to blanco excluding the non-realistic values, and Total 3 – total related to the initial leachate sample.**

Material	Total adsorption 1 (%)	Total adsorption 2 (%)	Total adsorption 3 (%)
01 – L/S=20	73.75	85.62	87.68
01 – L/S=50	68.97	70.38	82.98
10 – L/S=20	93.04	93.36	95.97
10 – L/S=50	79.31	79.52	87.88
05 – L/S=20	74.62	89.35	89.14
05 – L/S=50	34.02*	35.27*	61.12*
Green compost – L/S=20	91.55	95.42	97.61
Green compost – L/S=50	96.00	96.85	99.13
11 – L/S=20	42.38	42.38	77.09
11 – L/S=50	61.35	62.40	84.94

\*Low 'average' percentage, due to the bad adsorption of chloroethane.

### 5.3 Batch adsorption experiments – Part 2

Peat 05 and Green compost are chosen from the first adsorption experiments to do additional research on. After the first experiments, the adsorption capacity of peat 05 and green compost are further investigated with a benzene solution. These follow up experiments are done because of ambiguous results of the first experiments and to generate data on one component only (benzene) to be able to create a simplified (single-component) model. Additional material is ordered and green compost was sieved on 11.2 mm before the start of the experiments. Table 5.6 and 5.7 shows the percentage of dry weight of the materials. The dry weight is measured

several times and with two methods to ensure that the found percentages are significant for the material. The tests showed that differences were small and the average percentage of the two methods was 37.4 % dm for peat 05 and 59.9 % dm for green compost.

**Table 5.6 Percentage dry weight of the tested adsorption materials during the benzene adsorption test (determined with a *Sarorius MA 30* – moisture analyser at 105 °C).**

Test run	Peat 05 (% dm)	Green compost (sieved on 11.2 mm) (% dm)
1	38.9	59.2
2	38.8	61.2
3	36.8	58.7
4	38.3	60.2
<b>Average</b>	<b>38.2</b>	<b>59.8</b>

**Table 5.7 Percentage dry weight of the tested adsorption materials during the benzene adsorption test (determined with a carbolite furnace at 105 °C for 24 hr).**

	Peat 05	Green compost (sieved on 11.2 mm)
Wet sample weight (g)	44.29	76.31
Dry sample weight (g)	16.23	45.88
% dry material	36.6	60.1

An overview of the characteristics of the prepared batches for green compost is given in table 5.8. The exact L/S-ratio could only be determined after the batches were filled, because the volume which is occupied by peat is on forehand unknown. The cap of batch A turned out to be leaking, so this batch had to be stopped. The duplicates, batch D and E, show comparable equilibrium concentrations which indicate that the results of the experiment are reliable (table 5.9). The blanco concentration was found to be 1.1 mg/l, which is taken as initial concentration for the green compost experiments. The results are given in table 5.9 and figure 5.2 depicts the adsorption isotherm.

**Table 5.8 Characteristics of prepared batches to test the adsorption of benzene on green compost. Batch A was stopped, because of a leaking cap. In which  $M_s$  is the mass of dry soil;  $V_m$  is the volume of water as moisture in the material and  $V_w$  volume of added water. B is duplo of A and E is duplo of D.**

Batch	Wet sample (g)	$M_s$ (g)	$V_m$ (ml)	$V_w$ (ml)	Dilution	L/S-ratio
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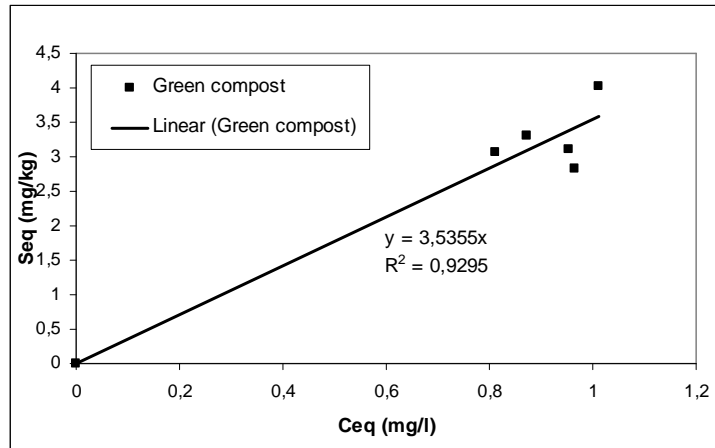
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A	39.961	23.965	15.996	Stopped	Stopped	Stopped
B	40.145	24.075	16.070	300.12	1.054	13.134
C	30.026	18.007	12.019	308.41	1.039	17.795
D	20.521	12.306	8.215	315.98	1.026	26.343
E	20.542	12.319	8.223	316.4	1.026	26.351
F	10.085	6.048	4.037	324.9	1.012	54.388
G	Blanco	Blanco	Blanco	333.51	Blanco	Blanco

The adsorbed percentages for green compost (table 5.9) are much lower than what was expected from literature and the previous batch experiments. For adsorption experiments it is desirable to be in the range of 50 – 80% adsorption, such that the upper part of the isotherm is determined. Adsorption percentages for these experiment range from 26.3% to 8%. Although the adsorbed percentage is low, a strong correlation between adsorbed amount and solute concentration is found. Besides that, there is a negative correlation between the L/S-ratio and the adsorption. Both indicate that the data is correct and reliable. The function of the adsorption isotherm is plotted in figure 5.2, it shows that  $K_d = 3.54$  l/kg.

**Table 5.9 Results of the batch experiments on green compost. The experiments are done at room temperature ( $\pm 20^\circ\text{C}$ ). In which  $C_0$  is the initial concentration, measured from the blanco batch;  $C_e$  is the equilibrium concentration and  $S_{eq}$  is the mass of adsorbed solute per unit mass of dry soil.**

Batch	$C_0$ (mg/l) (blanco)	$C_e$ (mg/l)	$S_{eq}$ (mg/kg)	Adsorbed (%)
B	1.100	0.770	3.058	26.3
C	1.100	0.840	3.310	20.7
D	1.100	0.940	2.837	12.3
E	1.100	0.930	3.109	13.3
F	1.100	1.000	4.029	8.0



**Figure 5.2 Linear adsorption isotherm of benzene on green compost.**

The experiments on peat 05 are done according to the same procedure as was followed during the experiments on green compost. Also, during this experiment one of the batches had to be stopped due to a leaking cap (batch F). Table 5.10 presents the characteristics of the batches. It can be noticed that the L/S ratio's were lower compared to the experiments on green compost. The lower ratio's are a direct result of the lower density of peat 05, due to which it was not possible to reach the same L/S ratio's. The blanco concentration was found to be 1.8 mg/l, which is taken as initial concentration for the peat 05 experiments. The results are given in table 5.11 and figure 5.3 depicts the adsorption isotherm.

**Table 5.10 Characteristics of prepared batches to test the adsorption of benzene on green compost. Batch F was stopped, because of a leaking cap. In which  $M_s$  is the mass of dry soil;  $V_m$  is the volume of water as moisture in the material and  $V_w$  volume of added water. B is duplo of A and E is duplo of D.**

Batch	Wet sample (g)	$M_s$ (g)	$V_m$ (ml)	$V_w$ (ml)	Dilution	L/S-ratio
A	30.651	11.470	19.181	266.870	1.072	24.940
B	30.829	11.536	19.293	278.620	1.069	25.824
C	15.225	5.697	9.528	304.130	1.031	55.055
D	7.372	2.759	4.613	317.370	1.015	116.720
E	7.812	2.923	4.889	317.400	1.015	110.250
F	39.450	14.762	24.688	Stopped	Stopped	Stopped
G	Blanco	Blanco	Blanco	335.080	Blanco	Blanco

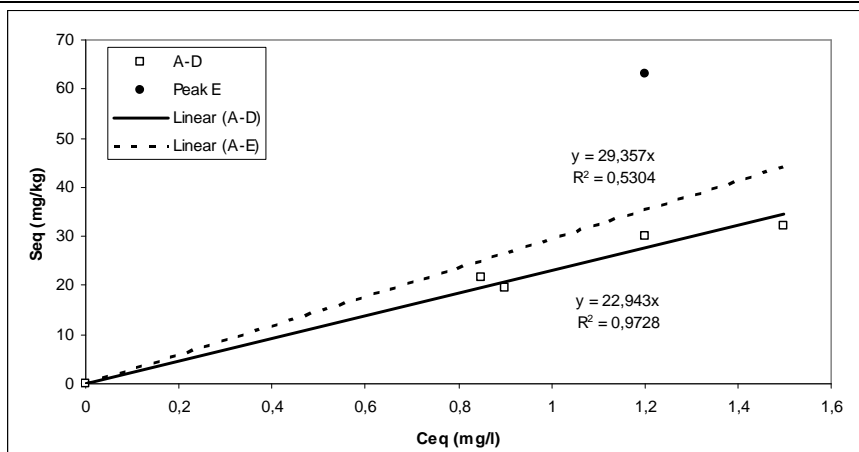
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**Table 5.11 Results of the batch experiments on peat 05. The experiments are done at room temperature ( $\pm 20^{\circ}\text{C}$ ). In which  $C_0$  is the initial concentration, measured from the blanco batch;  $C_e$  is the equilibrium concentration and  $S_{eq}$  is the mass of adsorbed solute per unit mass of dry soil.**

Batch	$C_0$ (mg/l) (blanco)	$C_e$ (mg/l)	$S_{eq}$ (mg/kg)	Adsorbed (%)
A	1.800	0.900	19.436	0.500
B	1.800	0.850	21.523	0.528
C	1.800	1.200	30.023	0.333
D	1.800	1.500	32.006	0.167
E	1.800	1.200	63.140	0.333

Figure 5.3 depicts two adsorption isotherms; one with all data and one excluding the deviating data point. One of the batches seemed to have adsorbed more than the other batches, due to which the correlation ( $R^2 = 0.53$ ) was weak. When this batch was excluded a very strong correlation was found ( $R^2 = 0.97$ ). The deviating batch could however be an indication of a higher adsorption potential of the peat, which would be in good agreement with the  $K_d$  value determined from the fraction of organic carbon that was found in the material (see next section). However, the fact that the duplicates are equal and the other two samples align with the data, indicates that the deviation is most likely a sampling or laboratory error.



**Figure 5.3 Linear adsorption isotherm for peat 05. The dashed line depicts the isotherm when the deviating point is included.**

Chapter 3.1 describes the theory behind adsorption of organic pollutants on organic material. In most cases the following function is used to estimate the  $K_d$ -value of a soil:

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

In which  $f_{oc}$  is the fraction of organic carbon and  $K_{oc}$  is the organic carbon partitioning coefficient of the contaminant. The  $f_{oc}$  of peat and green compost were determined because, the values which were found during the second batch experiment seemed to be low compared to the first batch experiment. The value of  $f_{oc}$  and  $K_{oc}$  can be used to determine the reliability of the second batch experiment. From literature it can be found that  $\log(K_{oc})$  of benzene varies between 1.7 and 2.0 l/kg. A LECO SC-632 (ASTM-approved) was used to measure the sulphur and carbon content of peat 05 and green compost. Peat 05 contained 47% of organic carbon and green compost 13.3%. The value of green compost is much lower than expected and probably explains the low adsorption. The low organic content could be a result of mixing the green waste material with inorganic matter, during the production process. The  $K_d$  values of benzene on peat varies (depending on  $K_{oc}$ ) between 23.5 and 47 l/kg and on green compost between 6.7 and 13.3 l/kg. These values are in the range of the values that were found during the experiment (22.94 and 3.54 respectively). The fact that the experimental values are somewhat lower than the calculated values, could be caused by limitations of the  $f_{oc}$  based formula, when high values of  $f_{oc}$  are concerned.  $f_{oc}$  is namely, a weight based parameter and adsorption is a surface process. Thus, at high  $f_{oc}$  values it is expected that relatively less adsorbs and that  $K_d$  becomes lower, which was also found for the batch experiments. So, the organic carbon content probably determines the adsorption capacity of the two materials, but it could overestimate the adsorption.

The  $K_d$  value for benzene adsorption on peat can also be compared to the data given by Cohen et al. (1991). Cohen et al. (1991) found  $K_d$  values ranging from 31.746 to 102.77 for  $f_{oc}$  values ranging from 0.51 to 0.54. This data seems to indicate that benzene adsorption onto peat can not only be determined from the organic carbon content. It has to be kept in mind however that Cohen et al. (1991) determined benzene adsorption from a saturated solution.

During the preparations of the experiments it turned out to be impossible, with an exception for the blanco's, to fill the batches without headspace. This was due to the structure of the material, which probably included air, although the 'wet' material was used. This was only enhanced by the fact that some part of the material floated on the water as a result of the low density. The headspaces will result in additional losses of benzene due to volatilization. However, the following worst case scenario calculations show that these losses are minimal and therefore negligible.

Using Henry's constant the concentration in the air can be calculated from the concentration in solution:

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$$M_g = V_a C_g = V_a H_{cc} C_w \text{ and, } M_w = V_w C_w \text{ and thus, } \frac{M_w}{M_g} = \frac{V_w}{(V_a H_{cc})}$$

In which  $M_g$  is the mass of benzene in the gas phase,  $C_g$  is the concentration in the gas phase,  $C_w$  is the concentration in the water,  $H_{cc}$  is henry's constant and  $M_w$  is the mass of benzene in the water. Taking;  $V_a = 10$  ml,  $V_w = 300$  ml and  $H_{cc} \approx 0.22$ , it is found that for every mass of benzene in the gas phase approximately 136 masses of solute are in the water phase. This means that volatilization inside the batches can be neglected.

## 5.4 Column experiments

### 5.4.1 Tracer experiment

The colour of the effluent was observed during the NaCl tracer experiment. It was noticed that especially the effluent of the green compost had a distinct dark colour (figure 5.4), which became darker over time. The effluent of the sand column was transparent and became cloudy white after which it became transparent again. The effluent of the peat started out with a light yellow transparent colour and ended with an orange transparent colour. Especially, the dark colour of the green compost has to be kept in mind when this material is used in the field situation.



**Figure 5.4 Color of effluents (from left to right: green compost, sand, peat) during the tracer experiment, with on the left picture the effluent of 10 April 2010 and on the right picture the effluent of 14 April 2010.**

Figure 5.5 and 5.6 depict the breakthrough curves of the tracer experiment. The figures show the rough data which were found during the experiment. From figure 5.6 it can be noticed that the conductivity which was measured after salt injection stopped (in the end about 1.5 mS/cm), became lower than the initial conductivity (about 6 mS/cm). This indicates that the influent demi water leaches the green compost from salts (or other conducting agents), which will in time result in a background conductivity of zero. Furthermore, the conductivity of the green compost effluent was higher at some points than the conductivity of the tracer fluid. This is also caused by the leaching of the green compost. To analyse the data and construct a  $C/C_0$  breakthrough curve, it was necessary to subtract the background conductivity from the measured conductivity, the function in figure 5.6 was used to do this. The background concentration of the peat and sand column were low at the start and it was therefore not necessary to take measures to construct a  $C/C_0$  breakthrough curve (see appendix 3 for calculations).

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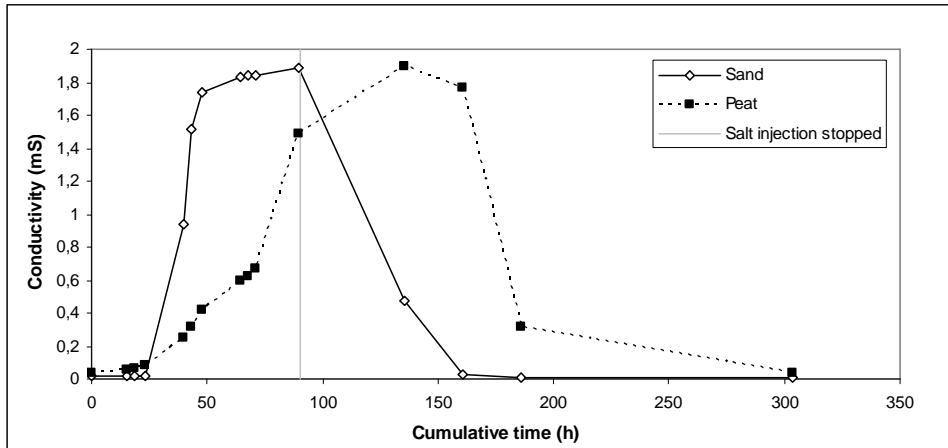


Figure 5.5 Breakthrough curve of NaCl measured as conductivity for the sand and peat columns.

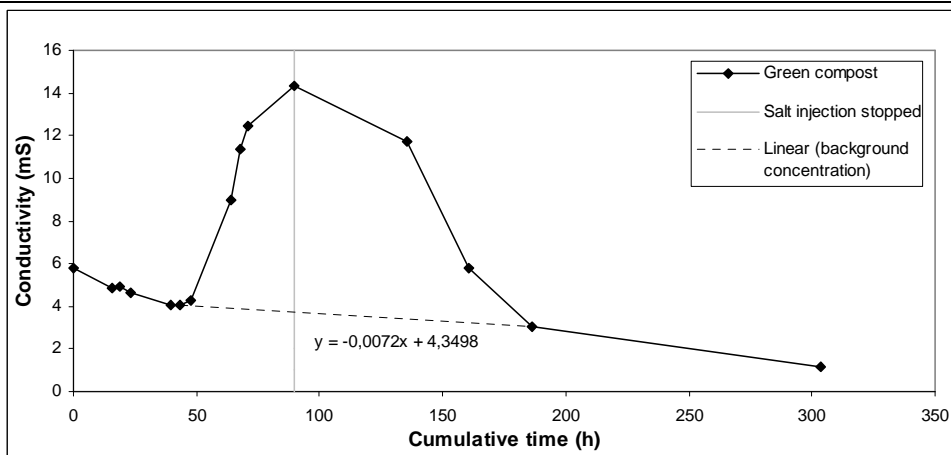


Figure 5.6 Breakthrough curve of NaCl measured as conductivity for the green compost column.

The experiment was continued until  $C/C_0 = 1$  was found, such that the data could be modelled with the 'continuous input in a semi-infinite domain – 'First type' boundary condition' modelling method. This was done by using the 1D internet model of the University of Illinois (Valocchi et al., 2003). With this model it is possible to fit the curve to the data (fig. 5.7), due to which  $v$ ,  $D$  (dispersion coefficient) and  $\theta$  can be determined (table 5.12). The data of peat 05 is described by two realizations. The data actually indicates that there could be two region flow, which results in 2 separate flows in the column (faster and slower). For this research it is however not necessary to go into detail about that. The two realizations can already be used to indicate the

sensitivity of the parameters, which is sufficient for this research. The porosity which is found by fitting the curve to the tracer data is called the calibrated porosity, and can be seen as the effective porosity. The porosity which is found in paragraph 4.3.1 is called the measured porosity, which is actually the total porosity.

The following flow and transport functions are used in the model of Valocchi et al. (2003): The governing equations consist of mass balance equations for adsorbed solute as well as dissolved solute (Hassanizadeh, 2007);

$$\frac{\partial \theta C}{\partial t} + \frac{\partial F}{\partial x} = -r_s$$

$$\frac{\partial (1-\theta)\rho^s s}{\partial t} = +r_s$$

Where  $r_s$  is the rate of sorption [ $M/L^3T$ ],  $F$  is the solute mass flux [ $M/L^2T$ ],  $s$  is the adsorbed concentration [ $M/M$ ],  $\theta$  is the effective porosity and  $C$  is the concentration of the solute [ $M/L^3$ ]. The sum of these equations and assuming an equilibrium linear adsorption isotherm yield;

$$\frac{\partial(\theta RC)}{\partial t} + \frac{\partial F}{\partial x} = 0$$

Where  $R$  is called the retardation factor and is defined by;

$$R = 1 + \frac{\rho_b}{\theta} K_d$$

For homogeneous media and for uniform velocity, the following equation can be written;

$$\frac{\partial C}{\partial t} + \frac{v}{R} \frac{\partial C}{\partial x} = \frac{D}{R} \frac{\partial^2 C}{\partial x^2}$$

In which the first term describes the concentration change in time, the second term describes the advective solute transport, and the third term describes the diffusion process. It is assumed that the input boundary is at  $x=0$  and that the system is infinitely long in the  $+x$  direction. Initially, there is a uniform concentration ( $C_0$ ) throughout the system and beginning at time  $t=0$  solute at concentration  $C_i$  is continuously fed into the column. The initial and boundary conditions can be established by a long-term input of solute at concentration  $C_0$  followed by a step change from  $C_0$  to  $C_i$  at time zero. Mathematically these initial and boundary conditions are expressed as (Valocchi et al., 2003);



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$$\begin{aligned}
 c(x, t = 0) &= C_0 \\
 c(x = 0, t) &= C_f \\
 c(x \rightarrow \infty, t) &= C_0
 \end{aligned}$$

The solution of the equation for the initial and boundary conditions yield;

$$\frac{c(x, t) - C_i}{C_f - C_i} = \frac{1}{2} \left[ \operatorname{erfc} \left[ \frac{x - \frac{v}{R}t}{2\sqrt{\frac{D}{R}t}} \right] + \exp\left(\frac{vx}{D}\right) \operatorname{erfc} \left[ \frac{x + \frac{v}{R}t}{2\sqrt{\frac{D}{R}t}} \right] \right]$$

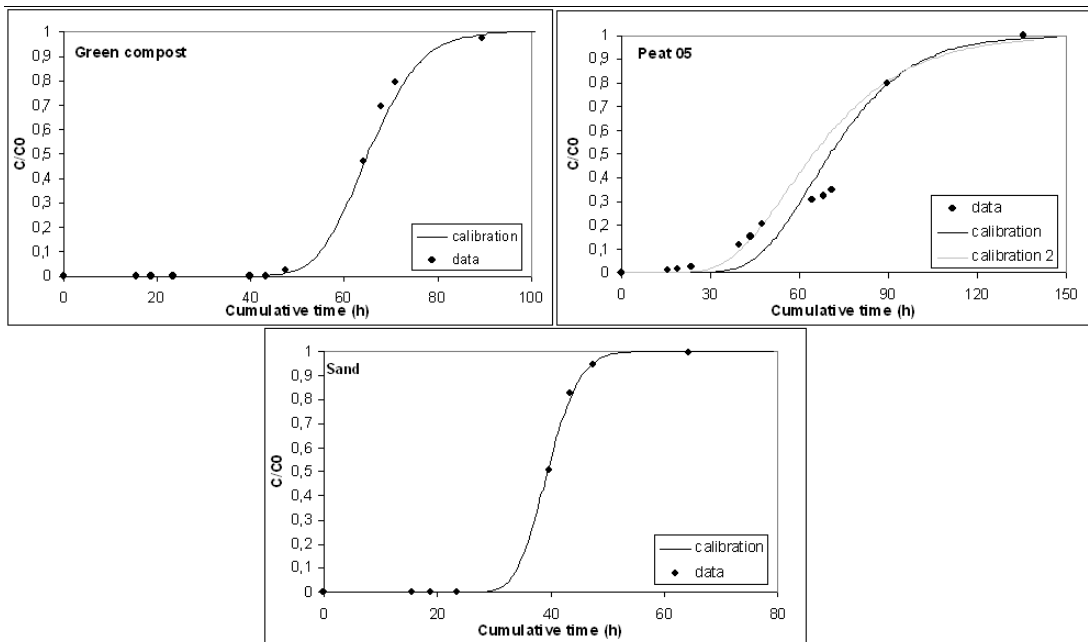


Figure 5.7 Calibration of the analytical solution for a breakthrough curve to determine the  $v$ ,  $\theta$  and  $D$ .

**Table 5.12 Difference between the measured and calibrated (effective) porosity. The calibrated porosity is calculated by fitting the tracer data with a breakthrough curve, from which  $v$  and  $D$  could be determined.  $Q$  is known and  $R=1$ , so by fitting the curve  $v$  could be used to calculate  $\theta$ .**

Material	$\theta_{\text{measured}}$	$\theta_{\text{calibrated}}^{\text{***}}$	$v_{\text{porewater}}$ (cm/hr)	$D$ (cm <sup>2</sup> /hr)
Peat	0.82	0.75* or 0.71**	0.68* or 0.72**	1.5* or 2.6**
Green compost	0.80	0.67	0.76	0.35
Sand	0.37	0.41	1.26	0.4

\* For peat calibration 1, \*\* For peat calibration 2, \*\*\* calibrated porosity  $\approx$  effective porosity.

Figure 5.8 shows the  $C/C_0$  versus normalized porevolume breakthrough curves. The normalized porevolume (dimensionless) is calculated with the following function:

$$\text{Porevolume} = \frac{t_c Q}{V \theta}$$

In which  $t_c$  is cumulative time,  $Q$  is the discharge,  $V$  is the volume and  $\theta$  is the porosity. A normalized porevolume of 1 indicates that the absolute porevolume has been flushed once. Figure 5.8 depicts the curve for both  $\theta_{\text{measured}}$  as  $\theta_{\text{calibrated}}$  to indicate the effect of the porosity on the breakthrough curve. The graph for peat 05 shows both calibrated porosities, it can be seen that the normalized porevolume becomes lower for higher porosity and thus breakthrough is later.

For a conservative tracer it is expected that  $C/C_0=0.5$  is found after 1 porevolume and is determined by the flow velocity in the column.  $C/C_0=1$  is influenced by the dispersion in the column and thus tells nothing about the flow velocity. In the graphs  $C/C_0=0.5$  is approximately found after 1 porevolume (for peat slightly later), which indicates the reliability of the tracer experiment.

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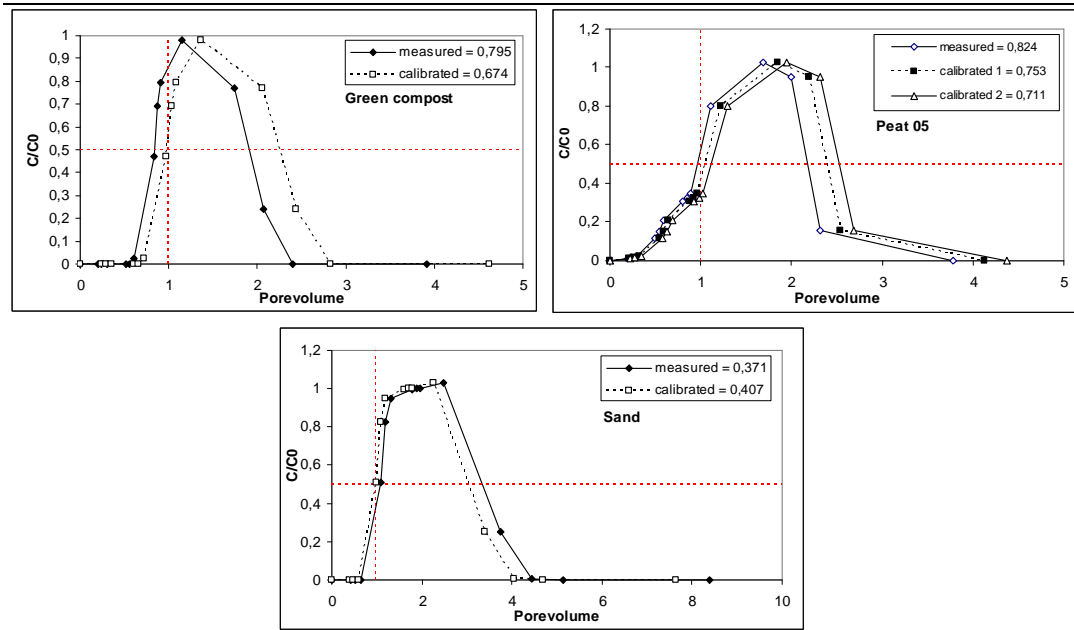


Figure 5.8 Breakthrough curve with C/C<sub>0</sub> versus normalized porevolume.

#### 5.4.2 Benzene adsorption experiment

The retardation factor is used to calculate the retardation of a contaminant with respect to the transport of a tracer. The retardation factor can be calculated from the  $K_d$  value by the following formula:

$$R = 1 + \frac{\rho_b}{\theta} K_d$$

Where  $R$  is the retardation factor,  $\rho_b$  the bulk density of the soil ( $\text{kg}/\text{dm}^3$ ),  $\theta$  the effective porosity of the soil, and  $K_d$  the distribution coefficient of the contaminant between the solid and the aqueous phase ( $\text{dm}^3/\text{kg}$ ). This equation is based on linear adsorption. Once the retardation factor is known, the average flow velocity of the contaminant ( $v_{\text{cont}}$ ) with respect to the groundwater flow ( $v_{\text{water}}$ ) can be determined by using:

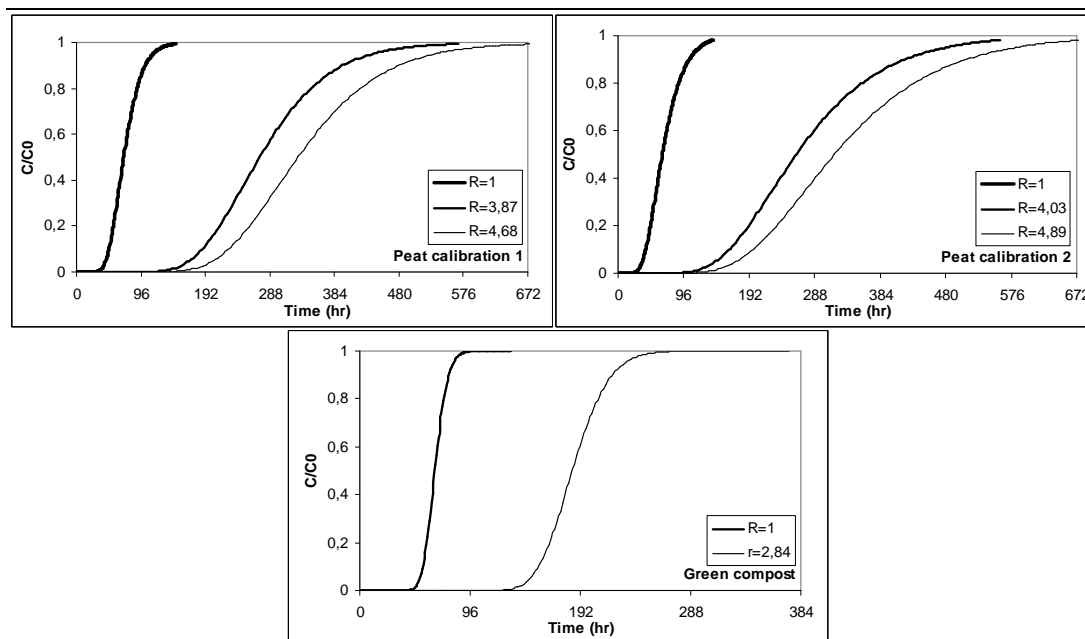
$$v_{\text{cont}} = \frac{v_{\text{water}}}{R}$$

The retardation coefficient and the velocity of the contaminant in the column can be estimated, by using this knowledge and the results of the tracer and batch experiments. Table 5.13 shows the calculated  $R$  values (for peat calculated with ranges of  $K_d$  and  $\theta$ ) and figure 5.9 shows the expected breakthrough curves following from this data. These results were used to design a sampling plan for the column adsorption experiments and are used for comparing the results of the batch experiments and the column experiments.

**Table 5.13** Calculation of the retardation coefficient in the peat and green compost columns.

Material	$K_d$ (l/kg)	$\theta$ (-)	$\rho_b$ (kg/dm <sup>3</sup> )	R
Peat*	22.9	0.75	0.094	3.87
Peat*	29.4	0.75	0.094	4.68
Peat**	22.9	0.71	0.094	4.03
Peat**	29.4	0.71	0.094	4.89
Green compost	3.5	0.67	0.353	2.84

\* For peat calibration 1, \*\* For peat calibration 2.

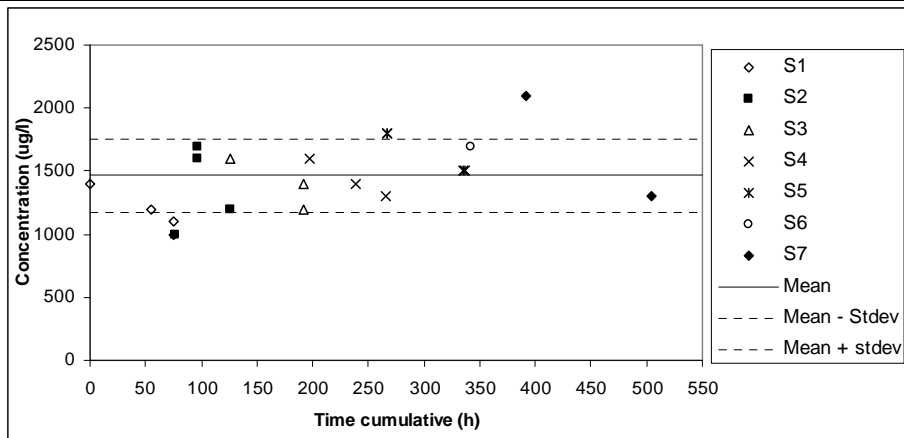
**Figure 5.9** Expected breakthrough curve for benzene in the peat and green compost column.

The influent stock solution was made with the essence to reach a concentration of approximately 2 mg/l, a concentration high enough for measurements and quite common in groundwater plumes like those from landfills. Figure 5.10 depicts however that this was not achieved. There are several trends visible in the figure, within a stock and between the stock solutions. In general, the concentration in a stock solution decreases in time and between the stock solutions the concentrations increase. The last trend is easily explained and is caused by differences in preparation. The first trend is however more difficult to explain. Fluctuation in organic contaminant concentrations is a well known phenomenon and is probably caused by the

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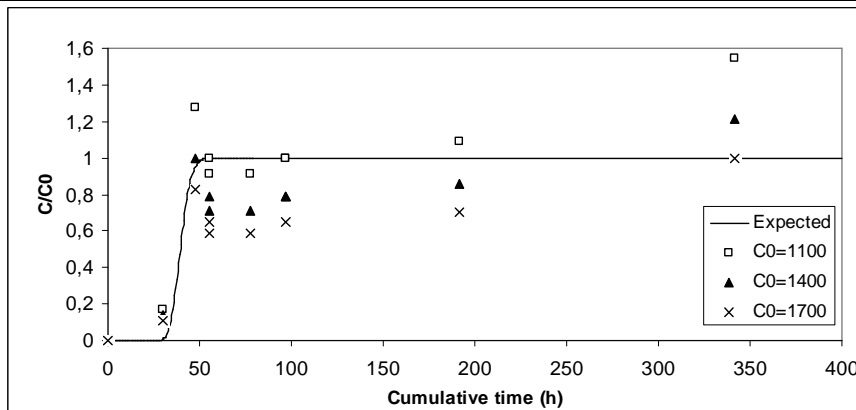
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hydrophobic character of these contaminants. Although benzene is quite soluble in water it rather sits at the glass walls of the stock jar than in the water, which will cause concentration differences in the water. Furthermore, volatilization losses will occur although argon pressure has been put on the solution.



**Figure 5.10 Concentrations of the different stock solutions in time.**

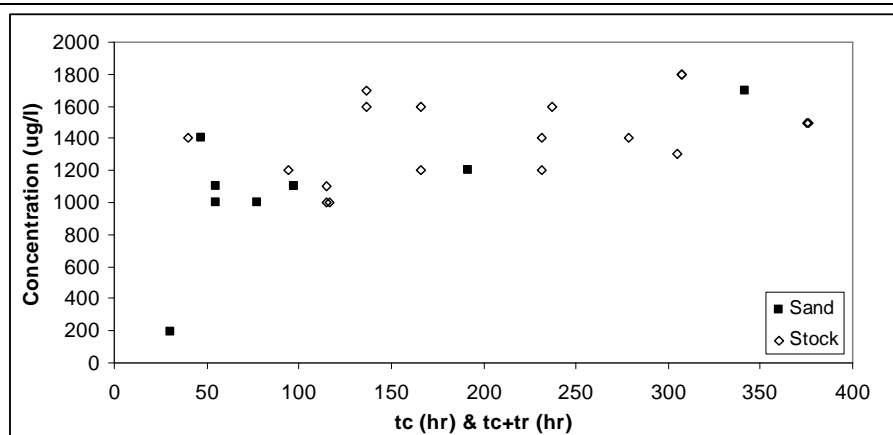
Figures 5.11, 5.13 and 5.14 give the results and the expected breakthrough curves of the sand, green compost and peat columns. The results are presented as dimensionless values ( $C/C_0$ ). The fluctuations in the influent concentrations make it difficult to calculate the breakthrough curve ( $C/C_0$  differs because  $C_0$  differs during the experiment). Therefore, the  $C_0$  was taken as average, average plus standard deviation and average minus standard deviation. This resulted in three breakthrough curves for every column and gives an indication of the sensitivity.



**Figure 5.11 Results of the sand column and expected breakthrough curve.**

The sand column is used as reference column for the green compost and peat column. Figure 5.11 already indicates that the results approximately follow the expected breakthrough curve. The variation around the expected curve is a direct result of the fluctuations in the inlet concentration  $C_0$ , figure 5.12 indicates this. Assuming that  $R=1$  and  $t_r \approx 39.7$  hr, the stock solution can be compared to the effluent concentration. There are some striking points in the graph which have to be explained. The lowest effluent concentration is a direct result of dispersion, due to which benzene is in the effluent before  $t_r$  is reached. Thereafter, a concentration of 1.4 mg/l is found after which the concentration decreases again to 1-1.1 mg/l. 1.4 mg/l is equal to the inlet concentration at  $t_c$ , but the dip is lower than the concentration trend of the stock solution, which reaches a minimal concentration of 1.2 mg/l. There are several explanations possible; 1) the influent concentration at that period is lower than reported, 2) the effluent concentration at that period is higher than reported, 3) breakthrough was not yet 100%. Explanation 1 and 2 are most likely, because from the tracer test breakthrough is expected to be approximately 100% after  $t_c=39.7$  hr and this is supported by the concentration of 1.4 mg/l before the dip. Furthermore, AL-west reports concentrations with only one decimal (rounding up or down of numbers), they state that more decimals will not make the results more accurate. This makes it impossible to give an exact interpretation of the data and therefore an approximation is necessary.

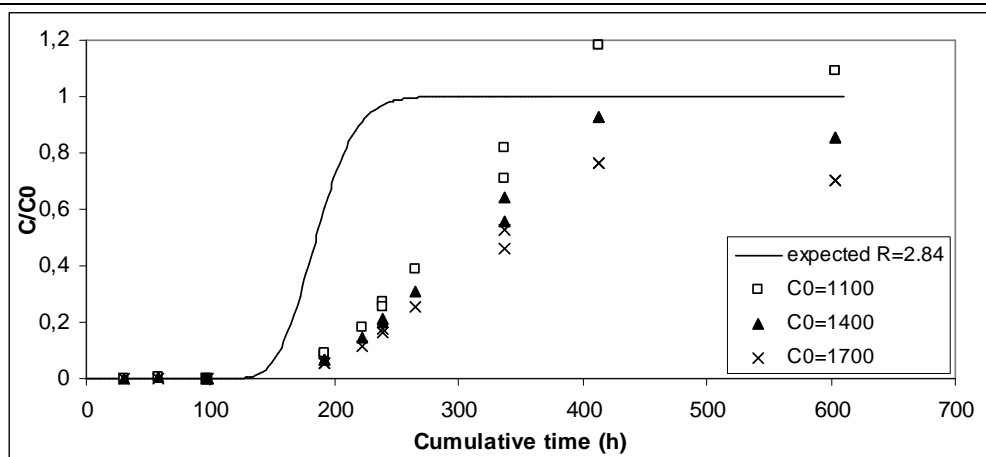
The results of figure 5.12 are also indicating that it is unlikely that aerobic biodegradation is taking place, because concentrations would be far lower if this was the case. Furthermore, similarity of the data indicates that assuming  $R=1$  is justified for the sand column.



**Figure 5.12 Comparison of the stock concentration with the effluent concentrations of the sand column. The x-as for the stock concentration is given as cumulative time + residence time in the sand column.**

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**Figure 5.13 Results of the green compost column and expected breakthrough curve.**

Figure 5.13 depicts that the found breakthrough of green compost column deviates from the expected column. Both, retardation and dispersion are higher than expected. The additional dispersion could indicate kinetic behaviour of the benzene. This could be a result of dead end pores (path length difference) and heterogeneities in the columns (heterogeneous particle sizes and pore sizes) or non-equilibrium adsorption. This effect is however not seen in the peat column, possibly due to a more homogenous particle distribution. The results of the peat column show that dispersion (fig. 5.14) is lower than expected from the tracer experiment. However, it is difficult to be certain because the column became clogged after approximately 400 hours. Therefore, the results of the last measurement are hard to validate. A water sample is taken from the top of the peat column to ensure that at least 50% breakthrough was reached and the results of the last samples (during flow) were not an error. A concentration of 1.2 mg/l was found, which is higher than the last sample and thus the last sample is assumed to be correct.

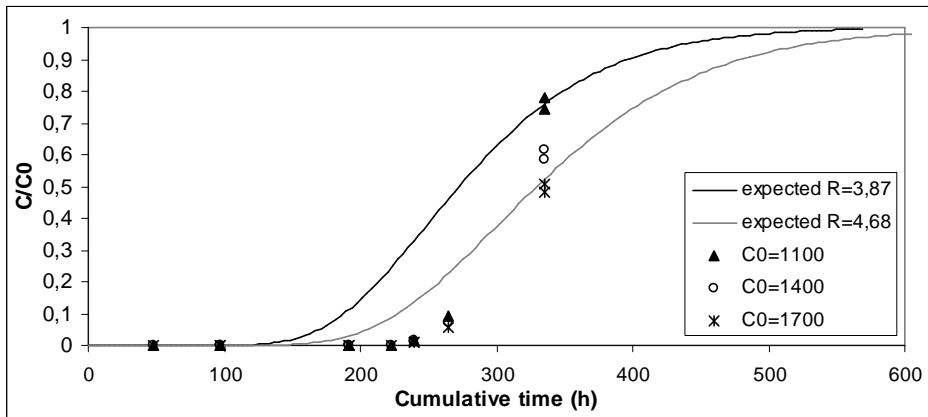


Figure 5.14 Results of the peat 05 column and expected breakthrough curve.

The data was again fitted by use of the 1D internet model of the University of Illinois (Valocchi et al., 2003) (fig. 5.15 and 5.16). The results are compared in table 5.14 for green compost and table 5.15 and 5.16 for peat 05. Two calibrations were done for peat, because this was also done for the peat tracer test.

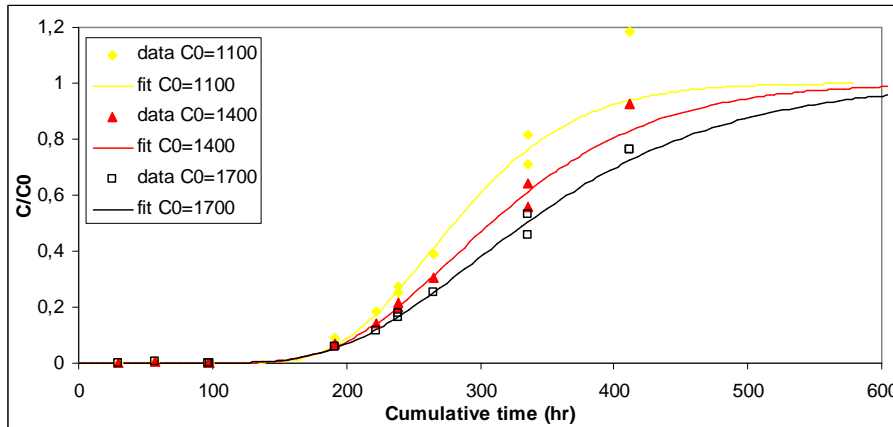


Figure 5.15 data and fit of the green compost column.

Table 5.14 Greencompost data fitted with the model of Valocchi et al. (2003), expected is the combined result of the batch and tracer experiment.

	Co=1100	Co=1400	Co=1700	Expected
Disp Coef (cm <sup>2</sup> /hr)	1.2	1.8	2.4	0.35



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R (-)	4.4	4.9	5.4	2.84
v (cm/hr)	0.76	0.76	0.76	0.76

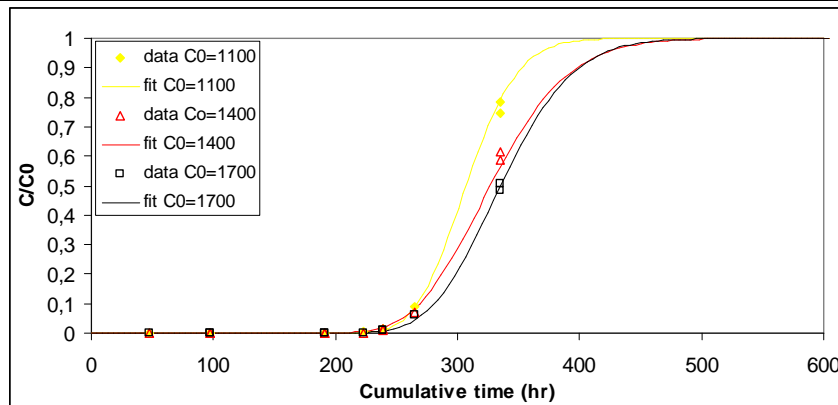


Figure 5.16 data and fit of the peat 05 column for calibration 1. data fit for calibration 2 are not shown because results are almost similar.

Table 5.15 Peat data fitted with the model of Valocchi et al. (2003), expected is the combined result of the batch and tracer experiment calibration 1.

	Co=1100	Co=1400	Co=1700	Expected
Disp Coef (cm <sup>2</sup> /hr)	0.2	0.4	0.32	1.5
R (-)	4.2	4.5	4.6	3.87-4.68
v (cm/hr)	0.68	0.68	0.68	0.68

Table 5.16 Peat data fitted with the model of Valocchi et al. (2003), expected is the combined result of the batch and tracer experiment calibration 2.

	Co=1100	Co=1400	Co=1700	Expected 2
Disp Coef (cm <sup>2</sup> /hr)	0.2	0.25	0.35	2.6
R (-)	4.5	4.7	4.9	4.03-4.89
v (cm/hr)	0.72	0.72	0.72	0.72

The retardation of benzene in the green compost column (4.4-5.4) is almost two times higher than what was expected from the batch experiments (2.84). The retardation of benzene in the peat column (4.2-4.9) is in the range of the expected retardation from the batch experiments (3.87-4.89). The retardation is however low compared to retardation factors calculated with  $K_d$

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values found by Cohen et al. (1991) which range between 5 and 15 for peat column characteristics (density and porosity). As told in Chapter 2 there are a lot of physical and chemical differences between several kinds of peat.

All the results of the laboratory analysis on which the figures are based are given in appendix 4. From the analysis it is noticed that the sand column or at least one of the tubes connecting the sand column was contaminated with toluene, because concentrations up to 370 µg/l are found. Besides that, small concentrations of xylene and ethylbenzene are found in the sand and green compost column. These concentrations could be due to impurities of the used benzene, which is not likely because these impurities were not found in the peat effluent. Ethylbenzene could also be formed in the green compost column from the interaction between benzene and possible present ethylene with minerals like zeolite as a catalyst.

## 6 Modelling and Case study

When studying the applicability of an adsorption drain as remediation technique a subdivisions in two scenarios has to be made; 1) the adsorption drain is used as stand-alone technique, and 2) the adsorption drain is one of several techniques combined for remediation of a site. The success of the drain will depend on several factors; 1) hydrological situation of the site, 2) contaminant situation and characteristics, 3) remediation objectives and legislation, and 4) drain dimensions and number of drains.

In scenario 1 the drain has to establish a complete hydraulic barrier which prevents the movement of contaminants downgradient of the drain. Scenario 1 is therefore a more demanding scenario than scenario 2 in which case contaminants moving downgradient are remediated by other techniques. This difference is essential, because it determines the discharge of the drain and thus the contaminant loading and its lifespan. The lifespan is especially important, because the runtime of the remediation will be endless due to the fact that the source is not remediated. The costs of the adsorption drain will therefore increase significantly when the lifespan is short. The discharge of the drain will also affect the residence time in the drain of contaminants which are not adsorbed, but could be aerobically degraded. A higher discharge leads to smaller residence times and less degradation.

### 6.1 2D sensitivity model

#### 6.1.1 Set-up and questions

The interception depth of the adsorption drain is an important design parameter when the drain is applied in the field. To get some insight in the effect of field and drain parameters a Modflow model has been used. Because, drain discharge is the most important and limiting factor it was important to construct the model in such way that this could be easily controlled. Modflow has a drainage package which could be used, but the discharge into the drain is hard to control because it depends on the factors which have to be changed in the analysis. Therefore, the well package is used and the drain bed is simulated as a thin layer beneath the well. When the conductivity of this layer is very low, the well will have no discharge. This represents a situation in which the necessary head gradient between the drain and aquifer to reach that specific discharge is so large that there is no more water in the drain to be pumped.

The boundary conditions for the model consist of a no-flow boundary at the bottom and constant-head boundaries at the left and right-hand sides. The constant-head boundaries are used to model a regional groundwater gradient. The upper boundary is unconfined with initially a linear head distribution. The grid system consists of 1 row and 202 columns. There are 30 layers

to a depth of 30 m. layer 1 is from 30 to 28.5 m, layer 2 from 28.5 to 28, layer 3 to 29 are each 1 m from 28 to 1 m and layer 30 is the no-flow boundary. The maximum interception depth is chosen to be 29 meter, because deeper contaminants are mostly not remediated, because human and ecological risks are often low and costs are high.

The well is placed in column 102 layer 1, the thickness of the drain bed is 0.5 m and simulated with a cell beneath the well in layer 2. Both cells are considered to be no-flow boundaries on the left and right hand-side to simulate the impermeable walls of the drain and prevent horizontal flow into the drain. The drain bed cell determines the conductance of the drain. Conductance is normally calculated by:

$$C_d = (K_{sd}Lw)/m$$

In which  $C_d$  is the drain conductance [ $L^2/T$ ],  $K_{sd}$  the conductivity of the drain bed material [ $L/T$ ],  $w$  the width of the drain channel [ $L$ ],  $L$  the drain channel length [ $L$ ] and  $m$  the thickness of the drain adsorption material [ $L$ ]. Figure 6.1 gives a simplified drawing of the cross-sectional model set-up.

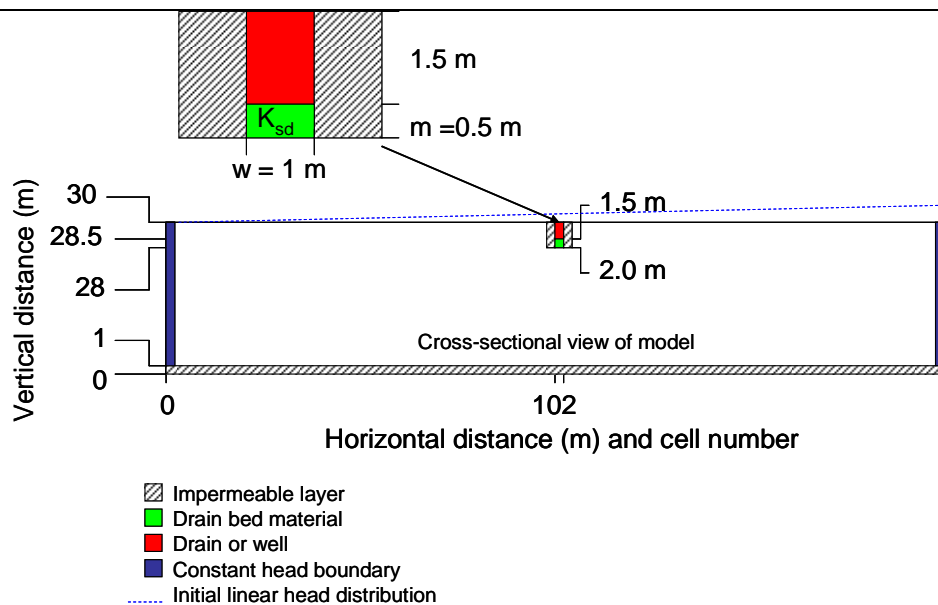


Figure 6.1 cross-sectional view of the model. The the width is 1 m, therefore a topview is not given.

In this model the conductance is varied by varying  $K_{sd}$ . The conductance, assuming that the discharge into the drain is equally distributed over the length of the drain, has no direct influence on the interception depth, but controls the working of the drain. A very low conductance will hamper the water to enter the drain. The lower limit of the conductance depends on the discharge of the drain.

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The drain discharge in the model can be seen as vertical groundwater flux into the drain (m/d), because it is a 2D model (1x1) m cell. Therefore, an increase in drain surface area can be modelled as an increase in the drain discharge ( $Q=A*q$ ). It could also be possible to increase the number of wells to simulate an increase in drain surface area, but results will be approximately the same. With two restrictions, namely: 1) the simulated surface area is not too large, and 2) the conductance is not a limitation for the simulated flux. When these conditions hold, the well represents the vertical discharge into the drain in  $m^2/d$ .

Important parameters are:

- Aquifer groundwater flux ( $G = K*i$ ) [L/T]
- Drain conductance ( $K_{sd}$ , drain vertical hydraulic conductivity)
- Drain discharge (Q)
- Anisotropy of the aquifer (r)

Important questions:

- What is the critical value for the conductance and its influence?
- What is the interception depth of the drain under varying parameters?
- What is the average residence time of the water in the drain?

### 6.1.2 Model results

For the construction of figure 6.2, 6.3 and 6.4 the situation of the landfill Kanaalpolder (described in chapter 6.2) was modelled with:  $G=0.002$  m/d,  $r=1$ ,  $\theta_e = 0.35$ , drain width is 1 m and drain depth = 1.5 m. Higher discharges than  $0.24$  m<sup>3</sup>/d are not relevant, because the discharge would be far higher than the natural groundwater discharge. Besides that, high discharges will have large drawdown effects on environment and agriculture, which it is not desirable.

Figure 6.2 depicts the model results for conductance versus drain discharge. Two drain bed thicknesses were modelled to verify  $C_d = (K_{sd}*L*w)/m$ . As expected, the difference between the resulting threshold- $K_{sd}$  is approximately the same as the ratio difference between the drain bed thicknesses.  $C_d$  plotted versus discharge gives therefore the same linear regression fit, which can be used for every drain dimension. The water level in the drain is directly affected by  $C_d$ , which is shown in figure 6.3. The difference between the peaks and the drain bed depth equals the necessary water level inside the drain to maintain  $q=0.0178$  m/d. When the drawdown is equal to the bed depth the discharge can not be kept constant anymore. The threshold line in figure 6.2 depicts the conductance at which this occurs for different discharges. In the model the discharge stops, in reality the discharge will reach a certain maximum. The most important influence of  $C_d$  on the drain is probably the effect on the residence time of the water in the drain (fig. 6.4).

When  $C_d$  decreases the residence time will also decrease, because the water level in the drain has to decrease to maintain a certain discharge. The residence time has a direct effect on the aerobic biodegradation potential and thus the effluent concentration of the drain. Modelling results show that the residence time becomes almost steady-state after a specific conductance has been reached (fig. 6.4). In other words, the effect is large at small conductance and small at large conductance.

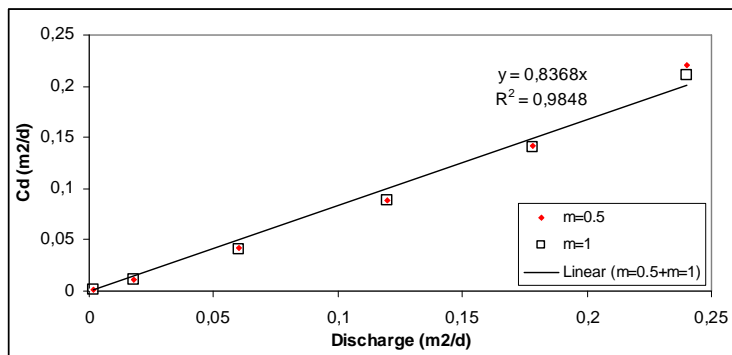
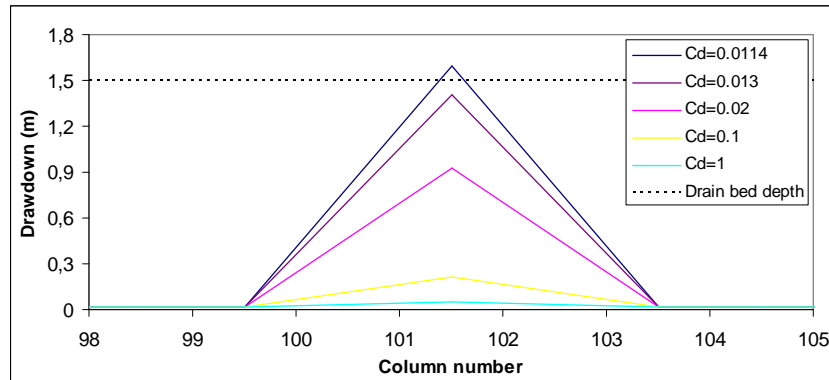


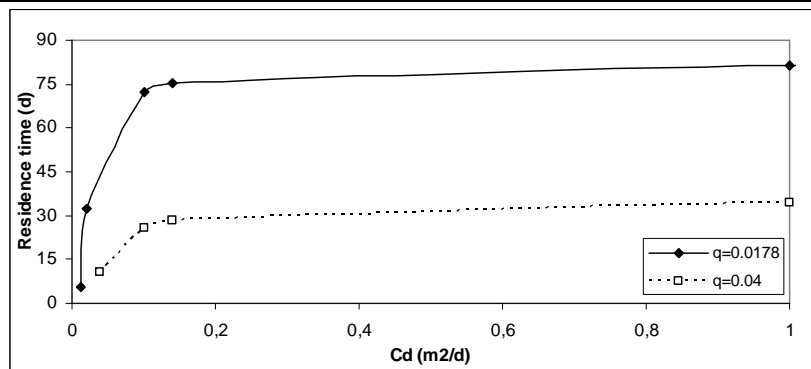
Figure 6.2 Limit of  $C_d$  versus drain discharge, modelled with the modflow well package. Drainage is possible above the line and stops below the line.  $C_d$  is calculated from  $K_{sd}$  by:  $C_d = K_{sd}/m$ .

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**Figure 6.3 Necessary drawdown at the drain to reach a discharge of 0.0178 m/d for varying  $K_{sd}$ , with a drain bed thickness of 0.5 m ( $K_{sd}=C_d*0.5$ ).**



**Figure 6.4 Influence of drain conductance on the residence time of water entering the drain, with a drain bed thickness of 0.5 m ( $K_{sd}= C_d/0.5$ ).**

The maximum residence time of water in the drain is determined by the drain discharge and drain depth (water depth). In this model the residence time is calculated by;

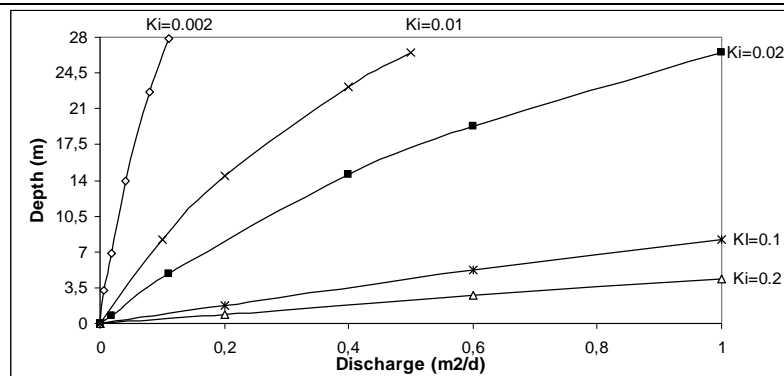
$$t_r = \frac{(d_0 - d_d)}{q}$$

Where  $d_0$  is the maximum drain water depth (1.5 m),  $d_d$  is the water level during discharge (m),  $q$  is the drain water flux (m/d) and  $t_r$  is the residence time (d). The maximum residence time is thus calculated by  $d_0/q$ .

For the following figures the hydraulic conductivity of the drain bed material was assumed to be 1 m/d. This conductivity was based on the conductivity experiments which are described in

chapter 5. The drainage depth is determined with the pmpath package of Modflow at 25 m upstream of the drain. This was done because near the drain the flow lines are radial instead of horizontal.

The effect of the natural groundwater flux on the capture depth for a specific discharge, is depicted in figure 6.5. It can be seen that, such as expected, the capture depth decreases if the groundwater flux increases. The difference is however not linearly distributed; a doubling in  $G$  does not result in a same decrease of capture depth. But, the difference becomes more linear at higher  $G$ .



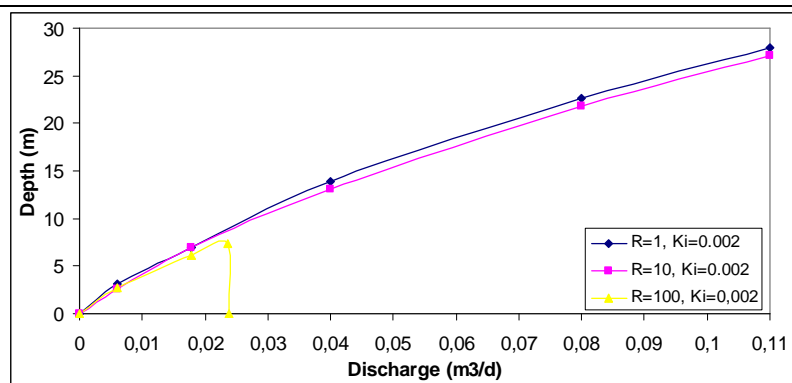
**Figure 6.5 Drainage depth versus discharge, each line depicts a specific natural groundwater flux. The anisotropy ratio ( $r$ ) is assumed to be 1.**

The effect of anisotropy on capture depth is minimal compared to the effect of the natural groundwater flux (fig. 6.6). The general trend is that at low discharge the capture depth is larger at higher anisotropy and at higher discharge this is other way around. Important to notice is that seepage to the drain stops at a certain discharge:anisotropy ratio; this is in agreement with was found in figure 6.2. This is different from findings of Zheng et al. (1988a), who found a large effect of anisotropy on capture depth. The difference is however that they kept a constant head in the drain, due to which discharge is directly affected by anisotropy and thus capture depth. In this research constant discharge is assumed, due to which anisotropy has a minimal effect on capture depth.



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**Figure 6.6 Combined effect of anisotropy and natural groundwater flux on capture depth for different discharges.**

The 1D sensitivity MODFLOW model, indicated that there is not one optimal drain dimension. Drain parameters, regional hydrological characteristics and contaminant characteristics are factors which have to be considered to design the optimal drain. For every situation the optimal drain situation has to be found. This paragraph could however be helpful to find the optimal dimensions, a construction plan is given below:

1. Determine regional hydrological characteristics; conductivity and regional gradient determine the groundwater flux, which has a significant effect on the drain interception depth.
2. Determine contaminant dimensions; the dimension of the plume determines the necessary interception depth.
3. Determine pollutant characteristics; the potential for adsorption and biodegradation differ for every pollutant, this affects the necessary thickness of adsorption material and the minimal residence time in the drain.
4. Determine the necessary drain discharge; from point 1 and 2 the discharge, which is needed to establish a hydrologic barrier for the contaminant, can be determined.
5. Determine the optimal conductance; this affects the residence time, the drain water level and the maximum possible discharge of the drain.
6. Conductivity, width and thickness of the bed adsorption material; these parameters affect the conductance of the drain bed. An optimal ratio between them has to be found. The thickness of the bed adsorption material should be as high as possible to enhance the adsorption potential.

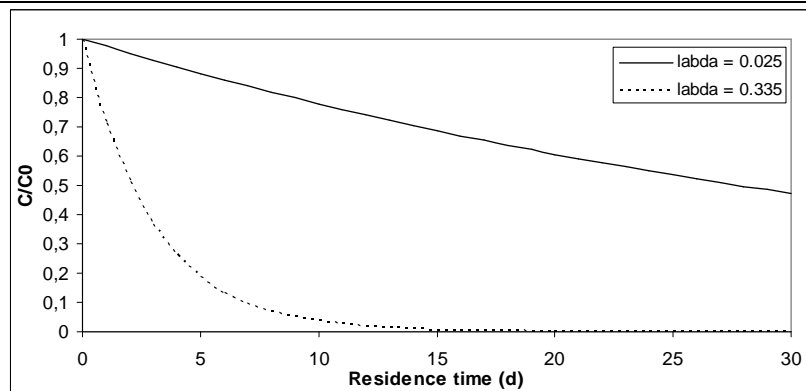
### 6.1.3 Drain surface water

Aerobic degradation rates for several organic contaminants in soils can be found in appendix 6. The first order degradation rate of benzene varies between  $0.025 \text{ d}^{-1}$  and  $0.335 \text{ d}^{-1}$ . Because,

there is no adsorption, degradation rates are expected to be high in aerobic surface water. The influent water is however anaerobic and therefore an aeration system could be necessary to reach aerobic conditions. The aerobic degradation curves for benzene is depicted in figure 6.7 and can be used to estimate the loss by biodegradation for a specific residence time. The curve is calculated with the first order decay formula:

$$C = C_0 e^{-\mu t}$$

Where C is the concentration in solution [M/L<sup>3</sup>], C<sub>0</sub> is the initial concentration [M/L<sup>3</sup>], μ is the first order decay rate coefficient [T<sup>-1</sup>], and t is time [T].



**Figure 6.7 First order degradation curve for two degradation constants of benzene.**

It is however questionable if degradation accounts for the most significant losses in the surface water, because of the volatility of benzene. Lyman et al. (1990) showed that the volatilization half-life of benzene from a model river (1 m deep, flowing 1 m/sec, wind velocity of 3 m/sec) is estimated as 1 hr ( $\lambda=24 \text{ d}^{-1}$ ). The volatilization half-life from a model lake (1 m deep, flowing 0.05 m/sec, wind velocity of 0.5 m/sec) is estimated as 3.5 days ( $\lambda=0.286 \text{ d}^{-1}$ ).

## 6.2 Landfill Kanaalpolder

At the moment Tauw bv is doing a pilot study of scenario 2 at the landfill Kanaalpolder north of Philippine (Zeeland, Netherlands). At the site a serious case of soil contamination has been indicated and therefore a remediation plan has to be submitted before 31 December 2010. The landfill is directly situated on top of a sandy soil and covers a surface of approximately 5 hectare. The most important contaminants in the groundwater beneath the plume are chlorinated solvents (VC and 1,1-dichloroethane) and aromatic compounds (benzene). The chlorinated solvents are found in the deep groundwater and the benzene in the shallow groundwater, which can be explained by density differences. The remediation plan distinguishes between the approach for 1) the landfill body, 2) the outgoing landfill leachate and 3) the plume. One of the

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remediation options is a risk reducing variant in which the site is treated by a natural approach, which consists of three steps:

1) Covering the landfill material with a layer of soil and organic material, this enhances biodegradation in the landfill and adsorbs volatile components. 2) Constructing a barrier system in which contaminated percolate is caught and purified. 3) Monitoring the natural attenuation process in the plume.

The adsorption drain can be implemented in step 2 as hydrological barrier for the landfill leachate. The drain lowers the groundwater table, due to which the seepage of contaminated groundwater in the ditches and at the groundwater surface will reduce. Also, the groundwater inside the landfill will lower, such that no lateral groundwater percolation will occur. Furthermore, the drain captures part of the contaminant source, due to which further spreading of the plume in the deeper groundwater is prevented or at least reduced.

In the situation of the Kanaalpolder landfill it is important that the discharge of the drain is as low as possible, because otherwise saltwater underlying the freshwater will enter the drain. The drain is used to control the site, thus only the natural groundwater flow has to be captured down to a certain depth.

The minimum discharge of the adsorption drain to control the landfill was calculated by assuming the following parameters (Boode, 2009):

- K (conductivity) 2 m/day
- D (thickness freshwater layer) 15 m
- i (gradient) 0.001 m/m
- a (direction of regional flow) WZW (205° with respect to east)
- s0 (groundwater table baseline situation) 0.5 m-gl

Furthermore, the drain has a depth of 3.2 m-gl, is 2.5 m wide, and a has total length of 450 m. Drainage of the drain is done by pumps which are placed in sections of hundred meter. Tripot was used to model the discharge of the drain, figure 6.8 shows that a discharge of, 20 m<sup>3</sup>/day (q = 0.0178 m/d) should be enough to control the landfill up to a depth of at least 14 m-gl. This is equal to the modflow results, which can be seen from figure 6.5 (at q=0.0445 m/d, because of the drain width in the field situation).

A limitation in this model is the lack of anisotropy and resistance of the drain bed. The previous paragraph showed however the influence of these variables. Anisotropy should not significantly decrease the drainage depth when the discharge is kept constant. The resistance of the drain bed is only important for the residence time of the contaminated water in the drain. Assuming  $K_{sd} \approx 1$  m/d and  $m = 0.5$  m the drain resistance is not affecting the residence time significantly.

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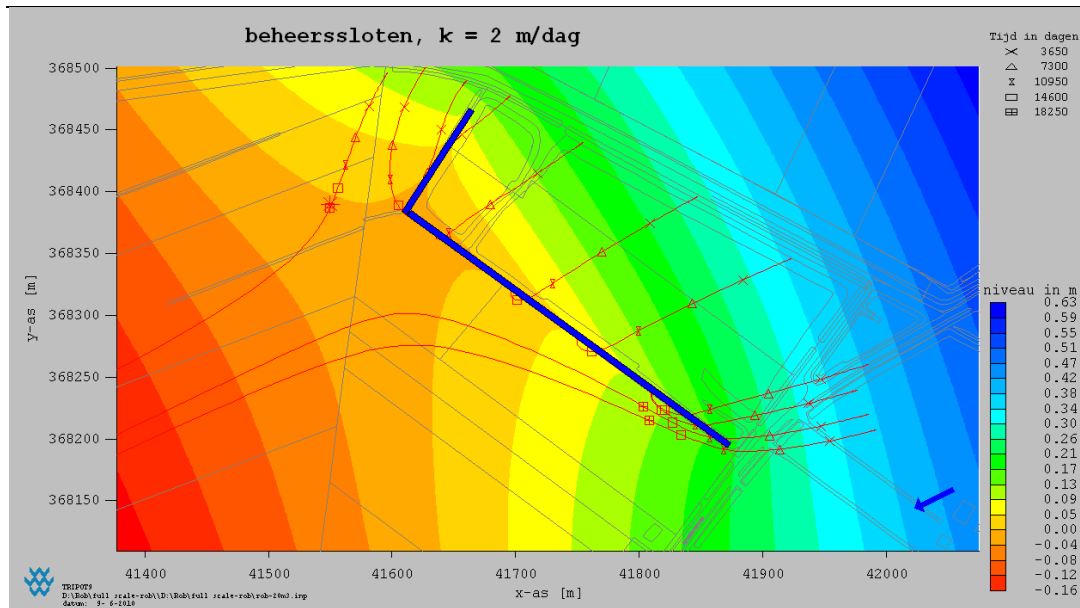


Figure 6.8 Streamline at 14 m depth for full scale drain with a total discharge of 20 m<sup>3</sup>/day (adjusted model of: Boode, 2009).

In the remediation plan it has been taken into account that the adsorption material should be refreshed once every five year. The batch and column experiments indicate however that this is an overestimation of the lifespan of the adsorption material. The following functions are used to calculate the lifespan of the adsorption material, the results are shown in table 6.1:

$$v_{water} = \frac{q_v}{\theta} = \frac{(Q/A)}{\theta}$$

In which  $v_{water}$  is the pore water velocity (m/d),  $q_v$  is the vertical groundwater flux (m/d),  $Q$  is the drain discharge (m<sup>3</sup>/d),  $A$  is the drain surface area (m<sup>2</sup>) and  $\theta$  is the material porosity.

$$t_r = \frac{m}{(v_{water}/R)}$$

In which  $m$  is the thickness of the sorption material in the drain (m) and  $R$  is the retardation factor.

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**Table 6.1 Calculation of the residence time (worst and best case) of benzene in the adsorption material.**

	<b>d (m)</b>	<b>θ (-)</b>	<b>R (-)</b>	<b>q (m/d)</b>	<b>v (m/d)</b>	<b>t<sub>r</sub> (d)</b>
Peat (best case)	0.5	0.75	4.9	0.018	0.024	103.35
Peat (worst case)	0.5	0.71	4.05	0.018	0.025	80.78
Compost (best case)	0.5	0.67	5.4	0.018	0.027	101.76
Compost (worst case)	0.5	0.67	2.84	0.018	0.027	53.59

The calculations show that whenever peat 05 is used as adsorption material in the adsorption drain at the Kanaalpolder landfill site, breakthrough of benzene will occur between 80 to 103 days. The lifespan of green compost has a larger range because of the unexpected results of the column experiment. For green compost benzene breakthrough will occur between 53 and 102 days. It has to be kept in mind however that breakthrough of other contaminants could be slower due to better adsorption onto the organic matter (see  $K_{oc}$ , appendix 6).

The lifespan of the adsorption drain can be increased by increasing the drain bed thickness. Figure 6.4 should be used to ensure that the residence time in the drain is not significantly decreased, but  $C_d$  is as low as possible. For a drain with  $q=0.0178$  m/d,  $C_d$  should be at least  $0.2$  m<sup>2</sup>/d, for a residence time of 75 days. The conductivity of the bed material was found to be  $0.46$  m/d for green compost and  $1.35$  m/d for peat, without limiting the residence time. Furthermore, biodegradation could further increase the lifespan of both materials.

According to chapter 2, aerobic biodegradation could occur in the upper 1 mm to 1.5 cm of the drain bed material due to oxygen penetration. If it is assumed that this will occur in the upper 1 cm of the drain bed, the maximum outlet concentration into the surface can be calculated with the following function:

$$C_{out} = C_0 e^{-\lambda t}$$

In which  $C_{out}$  is the concentration entering the surface water (ug/l),  $C_0$  is the initial concentration (ug/l),  $t$  is the residence time in the by oxygen penetrated layer (d) and  $\lambda$  is the first order biodegradation constant (d<sup>-1</sup>)

The rate of benzene biodegradation in an aerobic environment varies between  $0.025$  d<sup>-1</sup> and  $0.335$  d<sup>-1</sup>, according to appendix 6. If biodegradation could reach a degradation rate of  $0.335$  d<sup>-1</sup> it would have a big influence on the concentration entering the surface water. If  $C_0$  is assumed to be  $1000$  ug/l and residence times in the upper centimetre 2 days, degradation will reduce the

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concentration too 511.7 ug/l. The lower limit of the degradation rate does not significantly reduce the benzene concentration entering the surface water ( $C_{out} = 951$  ug/l).

It has to be kept in mind however that oxygen is consumed for aerobic biodegradation. This could lead to oxygen depletion in the peat, due to which biodegradation is slowed or even stopped. Furthermore, the water entering the drain will be anaerobe and it is therefore questionable if the surface water will be aerobic. Aeration of the water could be a necessity, but this could also lead to enhanced volatilization. Additional experiments have to be carried out to gain better insight in the biodegradation processes, which are important for the adsorption drain: 1) the interaction zone between ground and surface water, 2) stimulation of biodegradation due to the presence of organic material, 3) biodegradation versus volatilization in the surface water, 4) oxygen depletion due to organic matter degradation, 5) effect of aeration.

## 7 Discussion and conclusions

A literature review has indicated that peat and all sorts of modified forms have already been studied in the past as adsorption media for remediation purposes. Especially, the relatively low costs and high availability of peat and natural resources make it an interesting filter material. Most studies look however at **adsorption** of emulsified oils (from surface water or produced waste water) and not at contaminants in solution with groundwater (**adsorption**). In general, it can be said that peat adsorbs contaminants quite well, but data comparison is difficult because of differences in peat and contaminant characteristics. Therefore, it is essential to carry out adsorption experiments for every individual adsorption medium.

Fewer studies looked at the applicability of adsorbing drainage channels for the remediation of a contaminated site. Zheng et al. (1988a) developed a simple equation to estimate the interception depth of a drain (channel). Besides that, they indicated the effect of seasonal variation, which has a direct influence on the hydraulic head in the channel and the regional groundwater gradient. Furthermore, the effect of aquifer characteristics was modelled; a high conductivity layer can strongly decrease capture depth. The formula of Zheng et al. (1988a) did not apply to the model results of this thesis. Probably, because the assumption that  $l_w \ll 2H$  did not satisfy for the used model and conductance of the drain bed was not taken into account by Zheng et al. (1988a).

The use of organic material in an interceptor drain to adsorb dissolved contaminants has not been studied before on lab scale and in the field. Conductivity, batch and column experiments have been done to determine essential characteristics of potential adsorbents. A model is used to show aquifer and drain parameter effects on the sensitivity of such a remediation system. The combination of the results can be used for the design of a field scale adsorption drain remediation system.

Batch adsorption and conductivity experiments were carried out on 5 types of peat and green compost. The conductivities, determined with the constant head test, lay between 0.019 m/d (undisturbed peat) and 1.35 m/d (peat 05). A multi-component landfill leachate collected at Kanaalpolder (Zeeland, Netherlands) was used for the batch adsorption experiments. Results were however hard to interpret, because the initial concentrations could not be determined accurately enough. Due to this it was not possible to calculate  $K_d$  and retardation values from these data. The results of the batch and conductivity experiments were, however, used to select two materials for one-component experiments. Peat 05 and green compost were selected, because of their high hydraulic conductivities (1.35 and 0.46 m/d, respectively) and relatively good adsorption results.

Benzene was chosen as contaminant for the one component batch and column experiments. Because of the mobile character and persistency in anaerobic soils, benzene is often found in plume areas and is therefore a critical contaminant for the success of the adsorption drain. Furthermore, benzene was also found in the multi-component landfill leachate in Kanaalpolder.

From the benzene batch experiments  $K_d$  values could be determined. For green compost a  $K_d$  of 3.54 l/kg was found and for peat 05 a  $K_d$  of 22.9 to 29.4 l/kg. The variance in the  $K_d$  of peat is due to a deviating sample, which adsorbed relatively more than the other batches. It is therefore more likely that the  $K_d$  of peat is 22.9 l/kg. The  $K_d$  values were compared with Cohen et al. (1991), who found higher values (31.74 – 102.77 l/kg), but they looked at adsorption of benzene from a benzene saturated solution ( $\pm 1780$  mg/l compared to 1-2 mg/l in this thesis) in which absorption of free product probably took place as well..

The experimental  $K_d$  values were verified by determination of the organic carbon fraction in peat and green compost. From this fraction the  $K_d$  value can be approximated with literature values of  $K_{oc}$ . It was found that Peat 05 contained 47% of organic carbon and green compost 13.3%. The value of green compost was lower than expected and probably explains the low  $K_d$ . The low organic content could be a result of mixing the green waste material with inorganic matter, during the production process. The  $K_d$  values of benzene on peat varies (depending on  $K_{oc}$ ) between 23.5 and 47 l/kg and on green compost between 6.7 and 13.3 l/kg. These results are in the range of what was found from the batch experiments.

The batch experiments were used to estimate the retardation of benzene for the column experiments. Retardation is affected by the bulk density and porosity of the column material. These parameters can be influenced by the packing. Pressing more material in the column will increase the density and decrease the porosity, which results in an increase of the retardation factor. After packing of the columns, the retardation factor of peat and green compost were calculated from the batch data. Retardation factors were found to be, 3.84 – 4.89 for the peat column and 2.84 for the green compost column. These retardation factors were used together with the data from the column tracer test, to estimate the results of the benzene breakthrough curve.

The retardation factor was also calculated from the breakthrough curve data from a column experiment and compared with the expected breakthrough curve. Due to fluctuations of the influent concentration ( $C_0$ ), the retardation factor calculated from the column experiments was given as a range of values. The results of the peat column indicated a retardation factor between 4.2 and 4.9, which is equal to a  $K_d$  value between 24.2 and 31.1 l/kg. The results of the peat column are in good agreement with the results of the batch experiment. The retardation factor for



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the green compost was however found to be higher than expected, namely between 4.4 and 5.4 instead of 2.84. These retardation factors are equal to a  $K_d$  value between 6.45 and 8.35 l/kg. Although, this is not in agreement with the expected results from the batch experiment, it is still in the range of  $K_d$  values determined from the  $f_{oc}$  value for green compost.

During experimentation there have been some difficulties, which could have influenced the results. Air entrapment in the batches and the columns could have increased the total loss by volatilization instead of adsorption. Calculations have shown however, that losses will be small compared to accuracy of the analysis. Furthermore, the low density of green compost and particularly peat limited the amount of material which could be put in the batches. This led to low adsorption percentages (8-50%) where it is desirable to be in the range of 50 – 80% adsorption, such that the upper part of the isotherm is determined. On the other hand, the low density caused a desirable hydraulic conductivity.

The influent concentration of the columns could not be kept constant. Several stock solutions are prepared due to which differences in initial concentration occurred. Furthermore, the concentration of stock solution decreased in time, which was probably caused by volatilization and the hydrophobic effect of benzene. In the model constant concentration is assumed because a model with fluctuating influent concentrations did not give good results.

Another difficulty arose when the peat column clogged. Luckily, already 50-80% of the benzene was found in the last sample (verified with a sample taken from the top of the column with a syringe). However, because of the clogging the breakthrough curve of the peat column had to be interpolated.

There are some general problems which are encountered during the column experiments. Recommendations for future column adsorption experiments are therefore given in appendix 5.

Model results have indicated the sensitivity of hydrological and drain parameters on the drain interception depth and residence time. These results can be used for design purposes. The results reflect that it is not possible to give one good design. The necessary drain characteristics depend strongly on regional groundwater characteristics, which strongly affect interception depth. When the necessary drain discharge is found, the other dimensions can be determined from this, taking the conductance in mind. Conductance below a certain limit should be avoided, because this strongly decreases the residence time in the drain and thus the biological degradation in the surface water. When peat 05 or green compost is applied at the Kanaalpolder situation, the conductance will probably not influence the drain effectiveness, because of the relatively good hydrological conductivity of the materials.

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The experiments have shown that if a 0.5 m thick peat 05 layer is used as adsorption material in the adsorption drain at the Kanaalpolder landfill site, breakthrough ( $C/C_0=0.5$ ) of benzene is expected to occur at the latest after 103 days and at the earliest after 80 days. The lifespan of green compost has a larger range because of the unexpected results of the column experiment. For a 0.5 m thick green compost layer, benzene breakthrough will occur at the latest after 102 days and at the earliest after 53 days. It has to be kept in mind however that breakthrough of other contaminants could be later due to better adsorption (higher distribution coefficient) onto the organic matter (like monochlorobenzene, long chain aliphatics, PAH, PCE, pesticides, etc.). Furthermore, a lower drain discharge, thicker drain bed or higher density of the material could further increase the lifespan of the adsorption material.

Finally, it can be concluded that although the found retardation of benzene by peat 05 and green compost is not as high as expected, the adsorption drain could still be a working remediation technique. Because every contaminated site is different (f.i. composition of chemicals) and biodegradation has not been studied yet. Drain discharge, layer thickness and contaminant type have a significant influence on the lifespan of the adsorption material. For every site a model should determine if this lifespan is sufficient for continuing in construction of the drain. Biodegradation could further increase the lifespan and it is therefore recommended that follow up studies look at this. Furthermore, other remediation techniques could be applied in the channel (drain) as long as the drain captures the contaminant plume.

## Recommendations

The applicability of the adsorption drain is studied in this thesis by doing a literature review, conductivity and adsorption experiments and some modelling. Biodegradation experiments were not done, but are important. Therefore, it is necessary to do additional research upon this. In principle the same column setup could be used, with the addition of water in contact with the atmosphere above the organic material. Sampling ports in the organic layer should be used to track the pollutant in the adsorption material and the oxygen penetration. A distinction between degradation in and volatilization from the surface water has to be made, which could be quite a challenge. Furthermore, a sand column should be used as reference column to indicate any additional effect of the organic matter.

The adsorption experiments being done in this thesis had some limitations. In appendix 5 recommendations about the column set-up are given. There are however additional points of attention, which will be described here:

- More detailed analysis should be used; the accuracy given by AL-WEST is not detailed enough to give exact breakthrough curves. Also, more samples would facilitate in a more accurate breakthrough curve.
- More batch experiments; according to Cohen et al. (1991)  $K_d$  values of peat can be far higher than what was found during this thesis. A batch experiment is an easy method to find the best available adsorption material.
- A detailed tracer test; this forms the basis of a column experiment. Tracer breakthrough should therefore be monitored continuously, a computer could be used for this.



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# Appendix

## 1

Results and calculations of conductivity experiments

### Test – peat horizontal

Date	Time	Water (ml)
26-6-2009	7.30	start
26-6-2009	9.00	3.8
26-6-2009	10.00	6.4
26-6-2009	11.00	6
26-6-2009	12.00	6.6
26-6-2009	13.00	7.2
26-6-2009	14.00	7
26-6-2009	15.00	6.6
29-6-2009	7.00	439.8

	Difference in K (%)
Day 1 vs total	-14.01461867
After vs total	1.642338126
After vs day 1	18.20885894

	Water (ml)	Time (h)	Discharge (cm <sup>3</sup> /d)	K (cm/d)	K (m/d)
Total	483.4	71.5	162.2601399	1.932051531	0.019320515
Total day 1	43.6	7.5	139.52	1.661281876	0.016612819
Total after weekend	439.8	64	164.925	1.96378235	0.019637823

### Test – peat vertical

Date	Time	Water (ml)
26-6-2009	7.00	start
26-6-2009	9.00	7.8
26-6-2009	10.00	10.9
26-6-2009	11.00	10
26-6-2009	12.00	10.8
26-6-2009	13.00	11.7
26-6-2009	14.00	11.3
26-6-2009	15.00	10.7
29-6-2009	7.00	671.2

	Difference in K (%)
Day 1 vs total	-11.49919398
After vs total	2.236118927
After vs day 1	15.51998623

	Water (ml)	Time (h)	Discharge (cm <sup>3</sup> /d)	K (cm/d)	K (m/d)
Total	744.4	72	248.1333333	2.231759827	0.022317598
Total dag 1	73.2	8	219.6	1.975125436	0.019751254
Total after weekend	671.2	63.5	253.6818898	2.281664631	0.022816646

**Test – Peat 01**

date	Time	Water (ml)
21-9-2009	7.57	start
21-9-2009	8.11	431
21-9-2009	8.26	302
21-9-2009	9.07	459
21-9-2009	9.47	350
21-9-2009	12.03	805
21-9-2009	15.48	802
22-9-2009	8.00	restart
22-9-2009	10.00	207
22-9-2009	13.15	316
22-9-2009	15.30	179

	Water (ml)	Time (h)	Discharge (cm <sup>3</sup> /d)	K (cm/d)	K (m/d)
Total	3851	15.35	6021.107492	70.8793654	0.708793654
Total until restart	3149	7.85	9627.515924	113.3333394	1.133333394
Total after restart	702	7.5	2246.4	26.44420593	0.264442059

	Difference in K (%)
Before restart vs total	59.8960978
After restart vs total	-62.69124903
Before vs after	-76.66687837

**Test – Peat 02**

date	Time	Water (ml)
24-9-2009	6.45	start
24-9-2009	7.20	696
24-9-2009	8.03	527
24-9-2009	8.37	346
24-9-2009	9.44	543
24-9-2009	11.25	666
24-9-2009	13.00	502
24-9-2009	15.40	678
25-9-2009	6.45	restart
25-9-2009	8.50	407
25-9-2009	10.45	330
25-9-2009	11.50	98
25-9-2009	14.50	480

	Water (ml)	Time (h)	Discharge (cm <sup>3</sup> /d)	K (cm/d)	K (m/d)
Total	5273	17	7444.235294	80.53721769	0.805372177
Total until restart	3958	8.916666667	10653.30841	115.2553331	1.152553331
Total after restart	1315	8.083333333	3904.329897	42.23991511	0.422399151

	Difference in K (%)
Before restart vs total	43.10816344
After restart vs total	-47.552304
Before vs after	-63.35101035

**Test – Peat 10**

<i>date</i>	<i>Time</i>	<i>Water (ml)</i>
24-9-2009	6.45	start
24-9-2009	7.20	236
24-9-2009	8.03	431
24-9-2009	8.37	308
24-9-2009	9.44	558
24-9-2009	11.25	796
24-9-2009	13.00	664
24-9-2009	15.40	1030
25-9-2009	6.45	restart
25-9-2009	8.50	714
25-9-2009	10.45	605
25-9-2009	11.50	340
25-9-2009	14.50	895

	<i>Water (ml)</i>	<i>Time (h)</i>	<i>Discharge (cm<sup>3</sup>/d)</i>	<i>K (cm/d)</i>	<i>K (m/d)</i>
Total	6577	17	9285.176471	90.96388888	0.909638889
Total until restart	4023	8.916666667	10828.26168	106.0809986	1.060809986
Total after restart	2554	8.083333333	7583.010309	74.28831421	0.742883142

	<i>Difference in K (%)</i>
Before restart vs total	16.61880328
After restart vs total	-18.33208197
Before vs after	-29.97019714

**Test – Peat 05**

<i>date</i>	<i>Time</i>	<i>Water (ml)</i>
28-9-2009	9.45	start
28-9-2009	10.00	622
28-9-2009	10.25	970
28-9-2009	11.00	830
28-9-2009	11.55	1034
28-9-2009	13.45	restart
28-9-2009	14.55	966
28-9-2009	15.35	484
29-9-2009	6.45	restart
29-9-2009	7.30	483
29-9-2009	8.40	642
29-9-2009	9.55	715
29-9-2009	11.15	762
29-9-2009	13.05	1022
29-9-2009	15.05	1141

	<i>Water (ml)</i>	<i>Time (h)</i>	<i>Discharge (cm<sup>3</sup>/d)</i>	<i>K (cm/d)</i>	<i>K (m/d)</i>
Total	9671	12.33	18824.3309	189.2285119	1.892285119
Total until restart 1	3456	2.166666667	38281.84615	384.8220061	3.848220061
Total after restart 2	4906	4	29436	295.9005824	2.959005824
Total after restart 2	4765	8.33	13728.69148	138.0054288	1.380054288

	<i>Difference in K (%)</i>
Until rest. 2 vs total	56.37209182
After rest. 2 vs total	-27.06943185

### Test – Green compost

<i>date</i>	<i>Time</i>	<i>Water (ml)</i>
28-9-2009	9.45	start
28-9-2009	10.00	53
28-9-2009	10.25	137
28-9-2009	11.00	134
28-9-2009	11.55	189
28-9-2009	13.45	365
28-9-2009	14.55	234
28-9-2009	15.35	130
29-9-2009	6.45	restart
29-9-2009	7.30	181
29-9-2009	8.40	232
29-9-2009	9.55	242
29-9-2009	11.15	242
29-9-2009	13.05	346
29-9-2009	15.05	389

	<i>Water (ml)</i>	<i>Time (h)</i>	<i>Discharge (cm<sup>3</sup>/d)</i>	<i>K (cm/d)</i>	<i>K (m/d)</i>
Total	2874	14.16633333	4869.008683	49.8409313	0.498409313
Total until restart	1242	5.833	5110.234871	52.31020967	0.523102097
Total after restart	1632	8.333333333	4700.16	48.1125352	0.481125352

	<i>Difference in K (%)</i>
Before restart vs total	4.954318296
After restart vs total	-3.467824635
Before vs after	-8.02457971

### Test – Peat 11

<i>Date</i>	<i>Time</i>	<i>Water (ml)</i>	<i>K</i>
21-9-2009	7.57	start	n.v.t.
21-9-2009	7.57+33 sec	1000 ml	

The conductivity of this material was too high to measure with this experimental setup. The conductivity was also tested after the material was wetted for 1 day. But, this did not result in lower conductivities.

### Summary of calculations and column setup

Material	Specimen length (cm)	Head (cm)	Column length (cm)	Gradient (cm/cm)	K-total (m/d)	K-1e part (m/d)	K-2 <sup>e</sup> part (m/d)	Difference (total vs 2 <sup>e</sup> ) %
Peat horz.	11	32.5	43.5	3.95454	0.01932	0.016612	0.019637	1.642338126
Peat vert.	8.5	36	44.5	5.23529	0.02231	0.019751	0.022816	2.236118927
01	11.5	34.5	46	4	0.70879	1.133333	0.264442	-62.69124903
02	10.5	35.2	45.7	4.35238	0.80537	1.152553	0.422399	-47.552304
10	9.3	35.4	44.7	4.80645	0.90963	1.060809	0.742883	-18.33208197
05	9.5	35	44.5	4.68421	1.89228	2.959005*	1.380054	-27.06943185
Greencompost	10	36	46	4.6	0.49840	0.523102	0.481125	-3.467824635
11	10.8	34 - 0	-	-	-	-	-	-

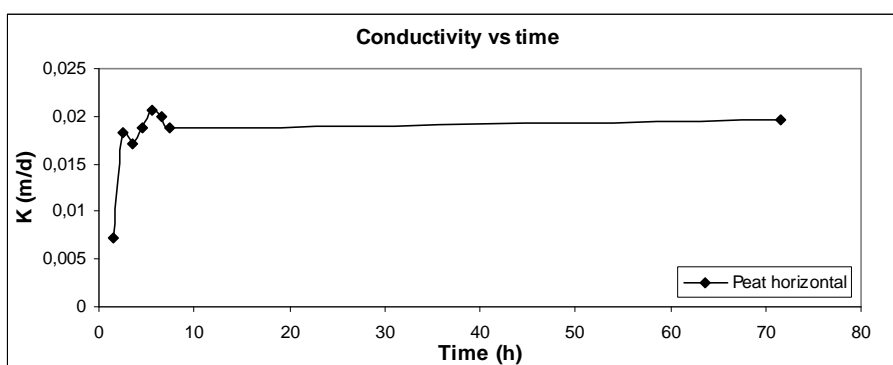
\* After a first restart



## Recalculations for 'static' conductivity

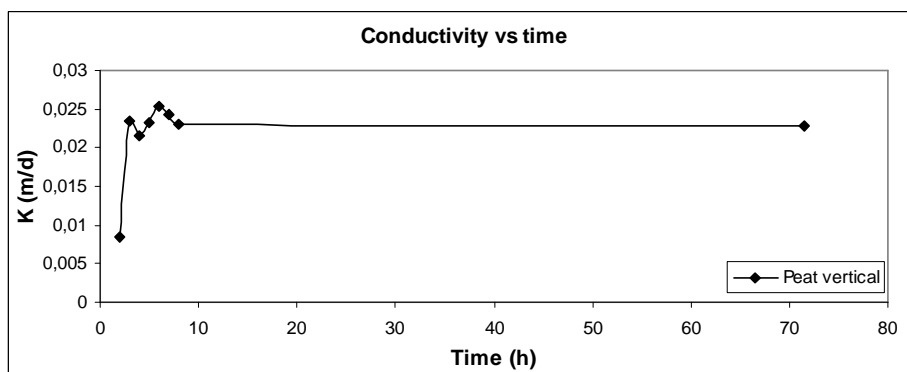
### Test – Peat horizontal

date	Time	Water (ml)	Time difference (h)	Discharge (cm <sup>3</sup> /d)	K (m/d)	Cumulative time (h)
26-6-2009	7.30	start				
26-6-2009	9.00	3.8	1.5	60.8	0.007239	1.5
26-6-2009	10.00	6.4	1	153.6	0.018287	2.5
26-6-2009	11.00	6	1	144	0.017144	3.5
26-6-2009	12.00	6.6	1	158.4	0.018858	4.5
26-6-2009	13.00	7.2	1	172.8	0.020573	5.5
26-6-2009	14.00	7	1	168	0.020001	6.5
26-6-2009	15.00	6.6	1	158.4	0.018858	7.5
29-6-2009	7.00	439.8	64	164.925	0.019635	71.5



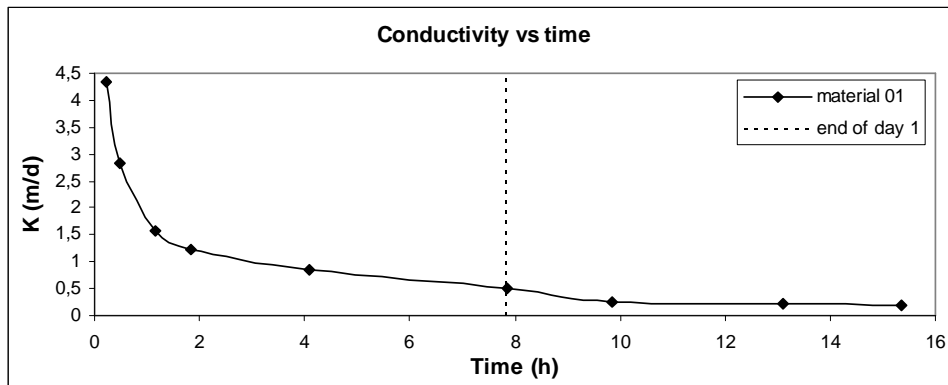
### Test – Peat vertical

date	Time	Water (ml)	Time difference (h)	Discharge (cm <sup>3</sup> /d)	K (m/d)	Cumulative time (h)
26-6-2009	7.00	start				
26-6-2009	9.00	7.8	2	93.6	0.008417	2
26-6-2009	10.00	10.9	1	261.6	0.023526	3
26-6-2009	11.00	10	1	240	0.021583	4
26-6-2009	12.00	10.8	1	259.2	0.02331	5
26-6-2009	13.00	11.7	1	280.8	0.025252	6
26-6-2009	14.00	11.3	1	271.2	0.024389	7
26-6-2009	15.00	10.7	1	256.8	0.023094	8
29-6-2009	7.00	671.2	63.5	253.6818898	0.022814	71.5



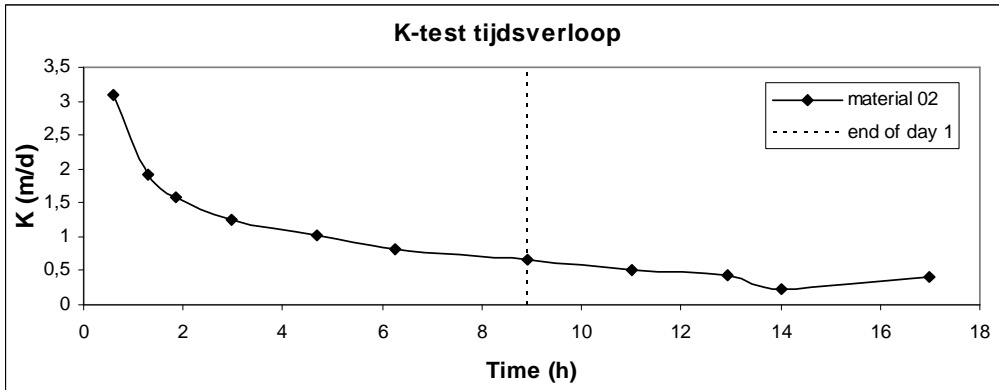
**Test – Peat 01**

date	Time	Water (ml)	Time difference (h)	Discharge (cm <sup>3</sup> /d)	K (m/d)	Cumulative time (h)
21-9-2009	7.57	start				
21-9-2009	8.11	431	0.233333333	44331.42857	4.342428133	0.233333333
21-9-2009	8.26	302	0.25	28992	2.839874114	0.483333333
21-9-2009	9.07	459	0.683333333	16120.97561	1.579109455	1.166666667
21-9-2009	9.47	350	0.666666667	12600	1.234216813	1.833333333
21-9-2009	12.03	805	2.266666667	8523.529412	0.834911373	4.1
21-9-2009	15.48	802	3.75	5132.8	0.50277683	7.85
22-9-2009	8.00	restart				
22-9-2009	10.00	207	2	2484	0.243317029	9.85
22-9-2009	13.15	316	3.25	2333.538462	0.228578762	13.1
22-9-2009	15.30	179	2.25	1909.333333	0.187026294	15.35



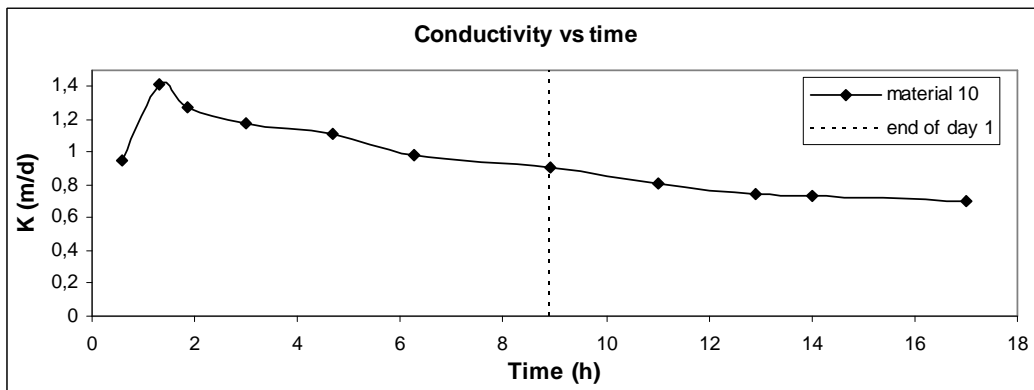
**Test – Peat 02**

date	Time	Water (ml)	Time difference (h)	Discharge (cm <sup>3</sup> /d)	K (m/d)	Cumulative time (h)
24-9-2009	6.45	start				
24-9-2009	7.20	696	0.583333333	28635.42857	3.097578	0.583333333
24-9-2009	8.03	527	0.716666667	17648.37209	1.909076	1.3
24-9-2009	8.37	346	0.566666667	14654.11765	1.585179	1.866666667
24-9-2009	9.44	543	1.116666667	11670.44776	1.262427	2.983333333
24-9-2009	11.25	666	1.683333333	9495.445545	1.02715	4.666666667
24-9-2009	13.00	502	1.583333333	7609.263158	0.823116	6.25
24-9-2009	15.40	678	2.666666667	6102	0.660071	8.916666667
25-9-2009	6.45	restart				
25-9-2009	8.50	407	2.083333333	4688.64	0.507184	11
25-9-2009	10.45	330	1.916666667	4132.173913	0.446989	12.916666667
25-9-2009	11.50	98	1.083333333	2171.076923	0.234852	14
25-9-2009	14.50	480	3	3840	0.415384	17



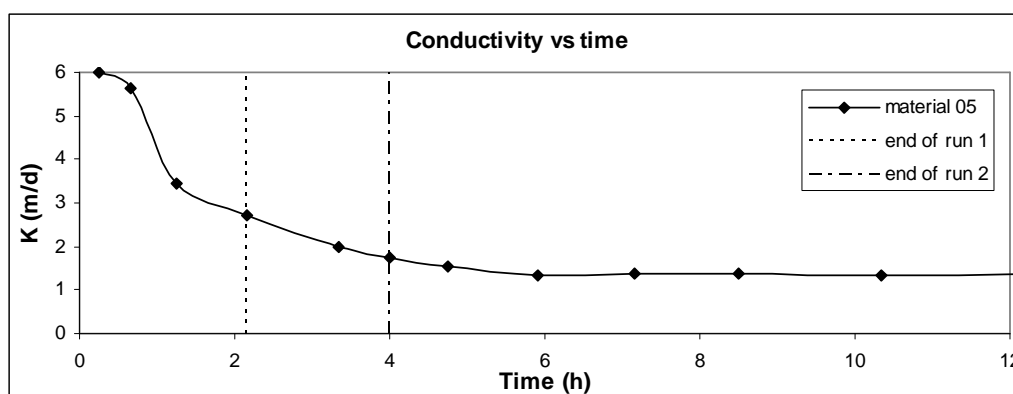
### Test – Peat 10

date	Time	Water (ml)	Time difference (h)	Discharge (cm <sup>3</sup> /d)	K (m/d)	Cumulative time (h)
24-9-2009	6.45	start				
24-9-2009	7.20	236	0.583333333	9709.714286	0.951102589	0.583333333
24-9-2009	8.03	431	0.716666667	14433.48837	1.413813811	1.3
24-9-2009	8.37	308	0.566666667	13044.70588	1.277777406	1.866666667
24-9-2009	9.44	558	1.116666667	11992.83582	1.174742826	2.983333333
24-9-2009	11.25	796	1.683333333	11348.91089	1.111667986	4.666666667
24-9-2009	13.00	664	1.583333333	10064.84211	0.985888678	6.25
24-9-2009	15.40	1030	2.666666667	9270	0.908030941	8.916666667
25-9-2009	6.45	restart				
25-9-2009	8.50	714	2.083333333	8225.28	0.805696735	11
25-9-2009	10.45	605	1.916666667	7575.652174	0.742063276	12.91666667
25-9-2009	11.50	340	1.083333333	7532.307692	0.737817523	14
25-9-2009	14.50	895	3	7160	0.701348601	17



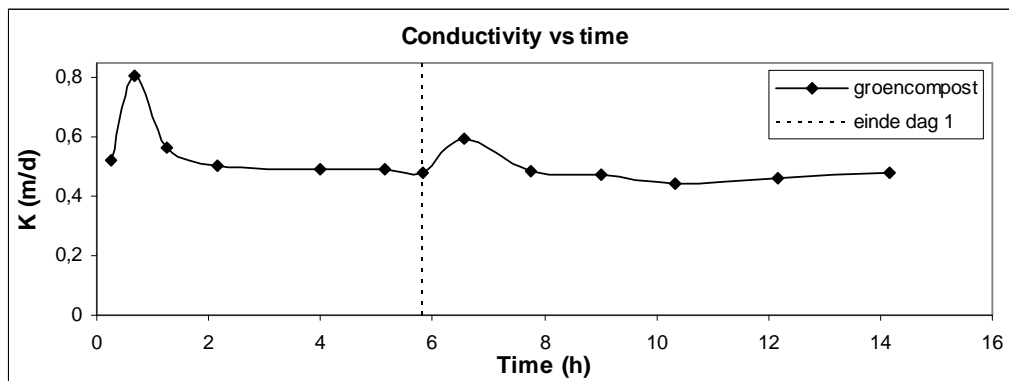
### Test – Peat 05

date	Time	Water (ml)	Time difference (h)	Discharge (cm3/d)	K (m/d)	Cumulative time (h)
28-9-2009	9.45	start				
28-9-2009	10.00	622	0.25	59712	6.00165	0.25
28-9-2009	10.25	970	0.416666667	55872	5.615692	0.666666667
28-9-2009	11.00	830	0.583333333	34148.57143	3.432271	1.25
28-9-2009	11.55	1034	0.916666667	27072	2.721006	2.166666667
28-9-2009	13.45	herstart				
28-9-2009	14.55	966	1.166666667	19872	1.997334	3.333333333
28-9-2009	15.35	484	0.666666667	17424	1.751285	4
29-9-2009	6.45	herstart				
29-9-2009	7.30	483	0.75	15456	1.553482	4.75
29-9-2009	8.40	642	1.166666667	13206.85714	1.327421	5.916666667
29-9-2009	9.55	715	1.25	13728	1.379801	7.166666667
29-9-2009	11.15	762	1.333333333	13716	1.378595	8.5
29-9-2009	13.05	1022	1.833333333	13378.90909	1.344714	10.33333333
29-9-2009	15.05	1141	2	13692	1.376182	12.33333333



### Test – Green compost

date	Time	Water (ml)	Time difference (h)	Discharge (cm3/d)	K (m/d)	Cumulative time (h)
28-9-2009	9.45	start				
28-9-2009	10.00	53	0.25	5088	0.520757	0.25
28-9-2009	10.25	137	0.416666667	7891.2	0.807664	0.666666667
28-9-2009	11.00	134	0.583333333	5513.142857	0.56427	1.25
28-9-2009	11.55	189	0.916666667	4948.363636	0.506465	2.166666667
28-9-2009	13.45	365	1.833333333	4778.181818	0.489047	4
28-9-2009	14.55	234	1.166666667	4813.714286	0.492683	5.166666667
28-9-2009	15.35	130	0.666666667	4680	0.478998	5.833333333
29-9-2009	6.45	herstart				
29-9-2009	7.30	181	0.75	5792	0.592811	6.583333333
29-9-2009	8.40	232	1.166666667	4772.571429	0.488472	7.75
29-9-2009	9.55	242	1.25	4646.4	0.475559	9
29-9-2009	11.15	242	1.333333333	4356	0.445836	10.33333333
29-9-2009	13.05	346	1.833333333	4529.454545	0.463589	12.16666667
29-9-2009	15.05	389	2	4668	0.47777	14.16666667





# Appendix

## 2

Results and calculation of adsorption – first batch experiments





Legend	
<b>Red</b>	Non-realistic value in comparison to concentrations found in the blanco
<b>Black</b>	Average 'total (1, 2, 3)' percentage
	Values for calculation of total 2

Contaminant	Blanco	01 - LS20			01 - LS50		
	$\mu\text{g/l}$	$\mu\text{g/l}$	$\mu\text{g/l after correction}$	% adsorption	$\mu\text{g/l}$	$\mu\text{g/l after correction}$	% adsorption
<i>Benzene</i>	68	27	31.306	53.961	52	54.942	19.203
<i>Toluene</i>	25	5.7	6.609	73.564	14	14.792	40.831
<i>Ethylbenzene</i>	980	160	185.519	81.0695	450	475.461	51.484
<i>Xylenes</i>	54	6	6.957	87.117	21	22.188	58.911
<i>C10-C40</i>	120	220	255.089	-112.574	90	95.092	20.756
<i>C10-C12</i>	55	0	0	100	20	21.132	61.579
<i>C12-C16</i>	33	0	0	100	0	0	100
<i>C16-C20</i>	11	0	0	100	7	7.396	32.763
<i>C20-C24</i>	13	8	9.276	28.646	9.1	9.615	26.039
<i>C24-C28</i>	6	20	23.190	-286.498	6.6	6.973	-16.224
<i>C28-C32</i>	0	140	162.329	error	38	40.150	error
<i>C32-C36</i>	0	27	31.306	error	6.5	6.868	error
<i>1.2 dichlorobenzene</i>	1.6	0	0	100	0	0	100
<i>1.4 dichlorebenzene</i>	2.2	0	0	100	0	0	100
<i>Monochlorobenzene</i>	50	7.1	8.232	83.535	23	24.301	51.397
<i>Naphtalene</i>	5.8	0	0	100	1	1.057	81.783
<i>Chloroethane</i>	2400	245	284.076	88.163	385	406.784	83.051
<b>Total</b>	3824.6	865.8	1003.890	<b>73.752</b>	1123.2	1186.752	<b>68.971</b>
		458.8	531.976	$\mu\text{g/l}$	1072.1	1132.760	$\mu\text{g/l}$
			3698.6	total $\mu\text{g/l}$		3824.6	total $\mu\text{g/l}$
			<b>85.617</b>	%		<b>70.382</b>	%

Contaminant	Leachate	01 - LS20			01 - LS50		
	$\mu\text{g/l}$	$\mu\text{g/l}$	$\mu\text{g/l after correction}$	% adsorption	$\mu\text{g/l}$	$\mu\text{g/l after correction}$	% adsorption
<i>Benzene</i>	140	27	31.306	77.638	52	54.942	60.756
<i>Toluene</i>	58	5.7	6.609	88.605	14	14.792	74.496
<i>Ethylbenzene</i>	2500	160	185.519	92.579	450	475.461	80.982
<i>Xylenes</i>	110	6	6.957	93.675	21	22.188	79.829
<i>C10-C40</i>	400	220	255.089	36.228	90	95.092	76.227
<i>Monochlorobenzene</i>	94	7.1	8.232	91.242	23	24.301	74.147
<i>Naphtalene</i>	10	0	0	100	1	1.057	89.434
<i>Chloroethane</i>	3000	245	284.076	90.531	385	406.784	86.441
<b>Total</b>	6312	670.8	777.789	<b>87.678</b>	1036	1094.618	<b>82.658</b>

	Total 1 (%)	Total 2 (%)	Total 3 (%)
01 - LS20	73.752	85.617	87.678
01 - LS50	68.971	70.382	82.658

Contaminant	Blanco	10 - LS20			10 - LS50		
	$\mu\text{g/l}$	$\mu\text{g/l}$	$\mu\text{g/l}$ after correction	% adsorption	$\mu\text{g/l}$	$\mu\text{g/l}$ after correction	% adsorption
Benzene	68	3.950	3.994	94.127	45.000	45.171	33.572
Toluene	25	0.000	0.000	100.000	9.900	9.938	60.250
Ethylbenzene	980	0.000	0.000	100.000	300.000	301.138	69.272
Xylenes	54	2.300	2.326	95.694	12.000	12.046	77.693
C10-C40	120	0.000	0.000	100.000	0.000	0.000	100.000
C10-C12	55	0.000	0.000	100.000	19.000	19.072	65.323
C12-C16	33	0.000	0.000	100.000	0.000	0.000	100.000
C16-C20	11	0.000	0.000	100.000	0.000	0.000	100.000
C20-C24	13	0.000	0.000	100.000	0.000	0.000	100.000
C24-C28	6	0.000	0.000	100.000	0.000	0.000	100.000
C28-C32	0	12.000	12.133	error	7.900	7.930	error
C32-C36	0	0.000	0.000	error	0.000	0.000	error
1,2 dichlorobenzene	1.6	0.000	0.000	100.000	0.000	0.000	100.000
1,4 dichlorobenzene	2.2	0.000	0.000	100.000	0.000	0.000	100.000
Monochlorobenzene	50	0.000	0.000	100.000	14.000	14.053	71.894
Naphtalene	5.8	0.000	0.000	100.000	0.600	0.602	89.616
Chloroethane	2400	245.000	247.717	89.678	380.000	381.442	84.107
<b>Total</b>	3824.6	263.250	266.170	<b>93.041</b>	788.400	791.391	<b>79.308</b>
		251.250	254.037	$\mu\text{g/l}$	780.500	783.461	$\mu\text{g/l}$
			3824.600	totaal $\mu\text{g/l}$		3824.600	totaal $\mu\text{g/l}$
			<b>93.358</b>	%		<b>79.515</b>	%

Contaminant	Leachate	10 - LS20			10 - LS50		
	$\mu\text{g/l}$	$\mu\text{g/l}$	$\mu\text{g/l}$ after correction	% adsorption	$\mu\text{g/l}$	$\mu\text{g/l}$ after correction	% adsorption
Benzene	140	3.950	3.994	97.147	45.000	45.171	67.735
Toluene	58	0.000	0.000	100.000	9.900	9.938	82.866
Ethylbenzene	2500	0.000	0.000	100.000	300.000	301.138	87.954
Xylenes	110	2.300	2.326	97.886	12.000	12.046	89.050
C10-C40	400	0.000	0.000	100.000	0.000	0.000	100.000
Monochlorobenzene	94	0.000	0.000	100.000	14.000	14.053	85.050
Naphtalene	10	0.000	0.000	100.000	0.600	0.602	93.977
Chloroethane	3000	245.000	247.717	91.743	380.000	381.442	87.285
<b>Total</b>	6312	251.250	254.037	<b>95.975</b>	761.500	764.389	<b>87.890</b>

	Total 1 (%)	Total 2 (%)	Total 3 (%)
10 - LS20	93.041	93.358	95.975
10 - LS50	79.308	79.515	87.890

Contaminant	Blanco	05 – LS20			05 – LS50		
		µg/l	µg/l	µg/l after correction	% adsorption	µg/l	µg/l after correction
Benzene	68	17.000	18.149	73.311	16.000	16.360	75.941
Toluene	25	0.600	0.641	97.438	0.000	0.000	100.000
Ethylbenzene	980	0.000	0.000	100.000	0.000	0.000	100.000
Xylenes	54	0.000	0.000	100.000	0.000	0.000	100.000
C10-C40	120	280.000	298.922	-149.101	78.000	79.754	33.538
C10-C12	55	0.000	0.000	100.000	16.000	16.360	70.255
C12-C16	33	0.000	0.000	100.000	0.000	0.000	100.000
C16-C20	11	0.000	0.000	100.000	0.000	0.000	100.000
C20-C24	13	7.400	7.900	39.230	0.000	0.000	100.000
C24-C28	6	18.000	19.216	-220.273	5.200	5.317	11.384
C28-C32	0	200.000	213.516	error	39.000	39.877	error
C32-C36	0	42.000	44.838	error	7.600	7.771	error
1,2 dichlorobenzene	1.6	0.000	0.000	100.000	0.000	0.000	100.000
1,4 dichlorobenzene	2.2	0.000	0.000	100.000	0.000	0.000	100.000
Monochlorobenzene	50	4.100	4.377	91.246	6.100	6.237	87.526
Naphtalene	5.8	0.000	0.000	100.000	0.000	0.000	100.000
Chloroethane	2400	340.000	362.976	84.876	2300.000	2351.719	2.012
<b>Total</b>	3824.6	909.100	970.535	<b>74.624</b>	2467.900	2523.395	<b>34.022</b>
		369.100	394.043	µg/l	2421.300	2475.747	µg/l
			3698.600	totaal µg/l		3824.600	totaal µg/l
			<b>89.346</b>	%		<b>35.268</b>	%

Contaminant	Leachate	05 – LS20			05 – LS50		
		µg/l	µg/l	µg/l after correction	% adsorption	µg/l	µg/l after correction
Benzene	140	17.000	18.149	87.037	16.000	16.360	88.314
Toluene	58	0.600	0.641	98.896	0.000	0.000	100.000
Ethylbenzene	2500	0.000	0.000	100.000	0.000	0.000	100.000
Xylenes	110	0.000	0.000	100.000	0.000	0.000	100.000
C10-C40	400	280.000	298.922	25.270	78.000	79.754	80.062
Monochlorobenzene	94	4.100	4.377	95.344	6.100	6.237	93.365
Naphtalene	10	0.000	0.000	100.000	0.000	0.000	100.000
Chloroethane	3000	340.000	362.976	87.901	2300.000	2351.719	21.609
<b>Total</b>	6312	641.700	685.065	<b>89.147</b>	2400.100	2454.070	<b>61.121</b>

	Total 1 (%)	Total 2 (%)	Total 3 (%)
05 - LS20	74.624	89.346	89.147
05 - LS50	34.022	35.268	61.121

Contaminant	Blanco	11 – LS20			11 – LS50		
		µg/l	µg/l	µg/l after correction	% adsorption	µg/l	µg/l after correction
Benzene	68	54.000	55.152	18.894	46.000	46.371	31.808
Toluene	25	17.000	17.363	30.549	13.000	13.105	47.581
Ethylbenzene	980	540.000	551.524	43.722	340.000	342.739	65.027
Xylenes	54	27.000	27.576	48.933	16.000	16.129	70.132
C10-C40	120	75.000	76.601	36.166	61.000	61.491	48.757
C10-C12	55	45.000	45.960	16.436	22.000	22.177	59.678
C12-C16	33	0.000	0.000	100.000	0.000	0.000	100.000
C16-C20	11	5.700	5.822	47.076	7.000	7.056	35.851
C20-C24	13	5.300	5.413	58.361	7.400	7.460	42.618
C24-C28	6	5.000	5.107	14.888	7.200	7.258	-20.967
C28-C32	0	0.000	0.000	error	7.700	7.762	error
C32-C36	0	0.000	0.000	error	0.000	0.000	error
1,2 dichlorobenzene	1.6	0.000	0.000	100.000	0.000	0.000	100.000
1,4 dichlorobenzene	2.2	0.000	0.000	100.000	0.000	0.000	100.000
Monochlorobenzene	50	28.000	28.598	42.805	18.000	18.145	63.710
Naphtalene	5.8	1.700	1.736	70.064	0.900	0.907	84.358
Chloroethane	2400	-	-	-	-	-	-
<b>Total</b>	3824.6	803.700	820.852	<b>42.380</b>	546.200	550.601	<b>61.350</b>
		803.700	820.852	µg/l	531.300	535.581	µg/l
			1424.600	totaal µg/l		1424.600	totaal µg/l
			<b>42.380</b>	%		<b>62.405</b>	%

Contaminant	Leachate	11 – LS20			11 – LS50		
		µg/l	µg/l	µg/l after correction	% adsorption	µg/l	µg/l after correction
Benzene	140	54.000	55.152	60.605	46.000	46.371	66.878
Toluene	58	17.000	17.363	70.064	13.000	13.105	77.406
Ethylbenzene	2500	540.000	551.524	77.939	340.000	342.739	86.290
Xylenes	110	27.000	27.576	74.931	16.000	16.129	85.337
C10-C40	400	75.000	76.601	80.850	61.000	61.491	84.627
Monochlorobenzene	94	28.000	28.598	69.577	18.000	18.145	80.697
Naphtalene	10	1.700	1.736	82.637	0.900	0.907	90.927
Chloroethane	3000	-	-	-	-	-	-
<b>Total</b>	6312	742.700	758.550	<b>77.097</b>	494.900	498.887	<b>84.937</b>

	Total 1 (%)	Total 2 (%)	Total 3 (%)
11 - LS20	42.380	42.380	77.097
11 - LS50	61.350	62.405	84.937

Contaminant	Blanco	Green compost – LS20			Green compost – LS50		
	µg/l	µg/l	µg/l after correction	% adsorption	µg/l	µg/l after correction	% adsorption
Benzene	68	23.000	23.389	65.605	11.000	11.072	83.718
Toluene	25	41.000	41.693	-66.772	1.300	1.308	94.766
Ethylbenzene	980	4.600	4.678	99.523	16.000	16.104	98.357
Xylenes	54	1.300	1.322	97.552	0.000	0.000	100.000
C10-C40	120	0.000	0.000	100.000	0.000	0.000	100.000
C10-C12	55	14.000	14.237	74.115	0.000	0.000	100.000
C12-C16	33	0.000	0.000	100.000	0.000	0.000	100.000
C16-C20	11	6.200	6.305	42.684	5.400	5.435	50.589
C20-C24	13	5.600	5.695	56.195	5.100	5.133	60.513
C24-C28	6	7.100	7.220	-20.333	5.800	5.838	2.703
C28-C32	0	7.500	7.627	error	12.000	12.078	error
C32-C36	0	0.000	0.000	error	0.000	0.000	error
1.2 dichlorobenzene	1.6	0.000	0.000	100.000	0.000	0.000	100.000
1.4 dichlorobenzene	2.2	0.000	0.000	100.000	0.000	0.000	100.000
Monochlorobenzene	50	8.100	8.237	83.526	0.000	0.000	100.000
Naphtalene	5.8	0.000	0.000	100.000	0.000	0.000	100.000
Chloroethane	2400						
<b>Total</b>	3824.6	118.400	120.401	<b>91.548</b>	56.600	56.969	<b>96.001</b>
		62.800	63.861	µg/l	44.600	44.891	µg/l
			1393.600	totaal µg/l		1424.600	totaal µg/l
			<b>95.418</b>	%		<b>96.849</b>	%

Contaminant	Leachate	Green compost – LS20			Green compost – LS50		
	µg/l	µg/l	µg/l after correction	% adsorption	µg/l	µg/l after correction	% adsorption
Benzene	140	23.000	23.389	83.294	11.000	11.072	92.092
Toluene	58	41.000	41.693	28.116	1.300	1.308	97.744
Ethylbenzene	2500	4.600	4.678	99.813	16.000	16.104	99.356
Xylenes	110	1.300	1.322	98.798	0.000	0.000	100.000
C10-C40	400	0.000	0.000	100.000	0.000	0.000	100.000
Monochlorobenzene	94	8.100	8.237	91.237	0.000	0.000	100.000
Naphtalene	10	0.000	0.000	100.000	0.000	0.000	100.000
Chloroethane	3000	-	-	-	-	-	-
<b>Total</b>	6312	78.000	79.318	<b>97.605</b>	28.300	28.484	<b>99.140</b>

	Total 1 (%)	Total 2 (%)	Total 3 (%)
GC - LS20	91.548	95.418	97.605
GC - LS50	96.001	96.849	99.140

Contaminant	Leachate	Undisturbed peat L/S=17.4			Undisturbed peat L/S=65.4		
		$\mu\text{g/l}$	$\mu\text{g/l}$	$\mu\text{g/l}$ after correction	% adsorption	$\mu\text{g/l}$	$\mu\text{g/l}$ after correction
<i>Benzene</i>	320	10	23.9	83.0	95	112.4	19.7
<i>Toluene</i>	140	2.8	6.7	89.7	29	34.3	47.2
<i>Ethylbenzene</i>	1800	26	62.1	93.0	260	307.5	65.4
<i>Xylenes</i>	100	0.72	1.7	96.6	13	15.4	69.8
<i>C6-C10</i>	3300	45	107.4	91.1	400	473.1	60.6
<i>C10-C40</i>	1090	0	0	100.0	315	372.6	66.0
<i>Creosoles</i>	840	45	107.4	86.1	480	567.8	26.7
<i>Fenoles</i>	130.6	0	0	100.0	26.9	31.8	57.2
<i>Dichloromethane</i>	30	0	0	100.0	13	15.4	25.0
<i>Monochlorobenzene</i>	540	8.9	21.2	92.9	96	113.6	62.2
<i>Dichlorobenzene</i>	20	0	0	100.0	0.8	0.9	92.7
<b>Totaal</b>	8311	138	330.4	<b>92.9</b>	1729	2044.7	<b>55.8</b>

# Appendix

## 3

Results and calculations of the tracer experiment

0-situation: at 6 april 2010 when column is flushed with demi water

	Ec (mS)	Ec (mS)	Ec (mS)
Green compost	5.84	5.8	5.77
Peat	0.035	0.038	0.038
sand	0.016	0.016	0.014

Tracer solutions

	Added salt (g/l)	Ec 6 April (mS)	Ec 9 April (mS)	Ec 12 April (mS)
Green compost	8.0790	10.8	11.93	11.44
Peat & sand	1.0305	1.72	1.82	1.81

Resulting electrical conductivities

Date	Sample time	Time	Cumulative (h)	Ec Greencompost (mS)	Ec Peat (mS)	Ec Sand (mS)
6-apr-10	16:30-17:30	17:00	0	5.803**	0.037**	0.015**
7-apr-10	8:00-9:00	8:30	15.5	4.87**	0.058	0.018**
7-apr-10	11:15-12:15	11:45	18.75	4.9**	0.064	0.017**
7-apr-10	16:00-17:00	16:30	23.5	4.64**	0.084	0.015**
8-apr-10	8:15-9:15	8:45	39.75	4.05**	0.249	0.94
8-apr-10	11:50-12:50	12:20	43.3333	4.04**	0.315	1.52
8-apr-10	16:00-17:00	16:30	47.5	4.25	0.414	1.736
9-apr-10	8:45-9:45	9:15	64.25	8.97	0.595	1.83
9-apr-10	12:30-13:30	13:00	68	11.37	0.626	1.84
9-apr-10	15:30-16:30	16:00	71	12.43	0.669	1.84
10-apr-10*	10:00-11:00	10:30	89.5	14.3	1.49	1.89
12-apr-10	7:50-8:50	8:20	135.333	11.71	1.9	0.47
13-apr-10	9:10-10:10	9:40	160.666	5.82	1.77	0.03
14-apr-10	11:00-12:00	11:30	185.999	3.02**	0.32	0.012**
19-apr-10	8:30-9:30	9:00	303.499	1.149**	0.037**	0.008**

\* At 11 o'clock the injection of the salt tracer stopped and injection with demi water was continued

\*\*These conductivities are the result of leaching from the material.




Calculation of  $Ec/Ec_0$ , with:  $Ec_0$  (Green compost) = 10.83;  $Ec_0$  (peat) = 1.82 and;  $Ec_0$  (sand) = 1.82. The background conductivity ( $Ec_b$ ) is determined from the previous table and subtracted from the measured conductivity ( $Ec_m$ ). A function of  $Ec_b$  in time is used for the Green compost case, in which  $Ec_b$  was largely affected by time due to leaching of the soil.  $(Ec_m - Ec_b)/Ec_0 = Ec/Ec_0 = C/C_0$ .

Cumulative (h)	$(Ec_m - Ec_b)/Ec_0$ : Green compost	$(Ec_m - Ec_b)/Ec_0$ : Peat	$(Ec_m - Ec_b)/Ec_0$ : Sand
0	0	0	0
15.5	0	0.011538	0
18.75	0	0.014835	0
23.5	0	0.025824	0
39.75	0	0.116484	0.508242
43.3333	0	0.152747	0.826923
47.5	0.022765	0.207143	0.945604
64.25	0.472048	0.306593	0.997253
68	0.696667	0.323626	1.002747
71	0.796953	0.347253	1.002747
89.5	0.984483	0.798352	1.03022
135.333	0.782151	1.023626	0.25
160.666	0.258642	0.952198	0.008242
185.999	0	0.155495	0
303.499	0	0	0

Calculation of  $E_{c_b}$  for green compost

Formula for background concentration of green compost

Cumulative (h)	$E_c$ (mS)
43.333	4.04
185.999	3.02

  $C_b(t) = -0,0072x + 4,3498$

Cumulative (h)	$E_c$ Measured (mS)	$E_{c_b}$ (mS)	$E_c$ Tracer (mS)	$(E_{c_m} - E_{c_b})/E_{c_0}$ : Green compost
0	5.803	5.803	0	0
15.5	4.87	4.87	0	0
18.75	4.9	4.9	0	0
23.5	4.64	4.64	0	0
39.75	4.05	4.05	0	0
43.3333	4.04	4.04	0	0
47.5	4.25	4.0078*	0.2422	0.022364
64.25	8.97	3.8872*	5.0828	0.469326
68	11.37	3.8602*	7.5098	0.693426
71	12.43	3.8386*	8.5914	0.793296
89.5	14.3	3.7054*	10.5946	0.978264
135.333	11.71	3.3754024*	8.334598	0.769584
160.666	5.82	3.1930048*	2.626995	0.242567
185.999	3.02	3.02	0	0
303.499	1.149	1.149	0	0

\*Calculated with the function for  $E_{c_b}$

# Appendix

## 4

Benzene concentrations of the column experiment



Stock number	Cumulative time (hr)	Benzene concentration (ug/l)	Additional (ug/l)
S1.1	0	1400	
S1.2	54.5	1200	
S1.3a	75.5	1000	
S1.3b	75.5	1100	
S2.1	76.5	1000	
S2.2a	97	1700	
S2.2b	97	1600	
S2.3	126	1200	
S3.1	126	1600	
S3.2a	191.5	1200	
S3.2b	191.5	1400	
S4.1	197.75	1600	
S4.2	239.25	1400	
S4.3	265.25	1300	
S5.1a	267.5	1800	(+5.1 xyleen)
S5.1b	267.5	1800	(+4.5 xyleen)
S5.2	335.25	1500	(+4.5 xyleen)
S5.3	336.25	1500	(+4.5 xyleen)
S6.1	341.5	1700	(+1.6 xyleen)
S6.2	383.75	1800	
S7.1	391.75	2100	
S7.2	503.75	1300	

Sand number	Cumulative time (hr)	Benzene concentration (ug/l)	Additional (ug/l)
ZA1	30	190	
ZA2	47.5	1400	
ZA3.a	55	1100	
ZA3.b	55	1000	(+4.7 ug/l toluene)
ZA4	77.75	1000	(+230 ug/l toluene)
ZA5.a	97.25	1100	(+320 toluene)
ZA5.b	97.25	1100	(+170 toluene)
ZA6	191.5	1200	
ZA7	341.5	1700	(+370 toluene & 4.4 xylene)

Compost number	Cumulative time (hr)	Benzene concentration (ug/l)	Additional (ug/l)
G1	30	2.1	(+4.1 ethylbenzeen)
G2	57.5	4.8	(+3.4 ethylbenzeen)
G2.a	97.25	<1.5	(+3.7 ethylbenzeen)

G2.b	98.25	1.5	(+5 ethylbenzeen)
G3.a	191.5	96	(+3.9 ethyl)
G3.b	191.5	97	(+4.2 ethyl)
G4	222.75	200	(+3.9 ethyl)
G5.a	239.25	300	(+4.3 ethyl)
G5.b	239.25	280	(+4.2 ethyl)
G6	265.25	430	(+4.2 ethyl)
G7.a	336.25	780	(1.9 tol & 3.9 ethyl)
G7.b	336.25	900	(5 toluene)
G8.a	412.25	1300	(+4.2 ethyl)
G8.b	412.25	1300	(+4.2 ethyl)
G9	509.25	1200	(+3.6 ethyl)
CK1	603.25	1200	(te hoge rapportagegrens
CK2	603.25	1200	(te hoge rapportagegrens

Peat number	Cumulative time (hr)	Benzene concentration (ug/l)	Additional (ug/l)
V1	47.5	<1.5	
V2.a	97.25	<1.5	(+1.7 ethylbenzeen)
V2.b	97.25	<1.5	
V3.a	191.5	<1.5	
V3.b	191.5	<1.5	
V4	222.75	2.6	
V5.a	239.25	15	
V5.b	239.25	18	
V6	265.25	100	
V7.a	335.25	860	
V7.b	335.25	820	
Column became clogged ( $\pm$ 400 uur)			
VV**	"603.25"	1200	

\*\*This sample is taken with a syringe from the top of the peat column to verify V7. The column was already clogged for approximately 270 hours.

# Appendix

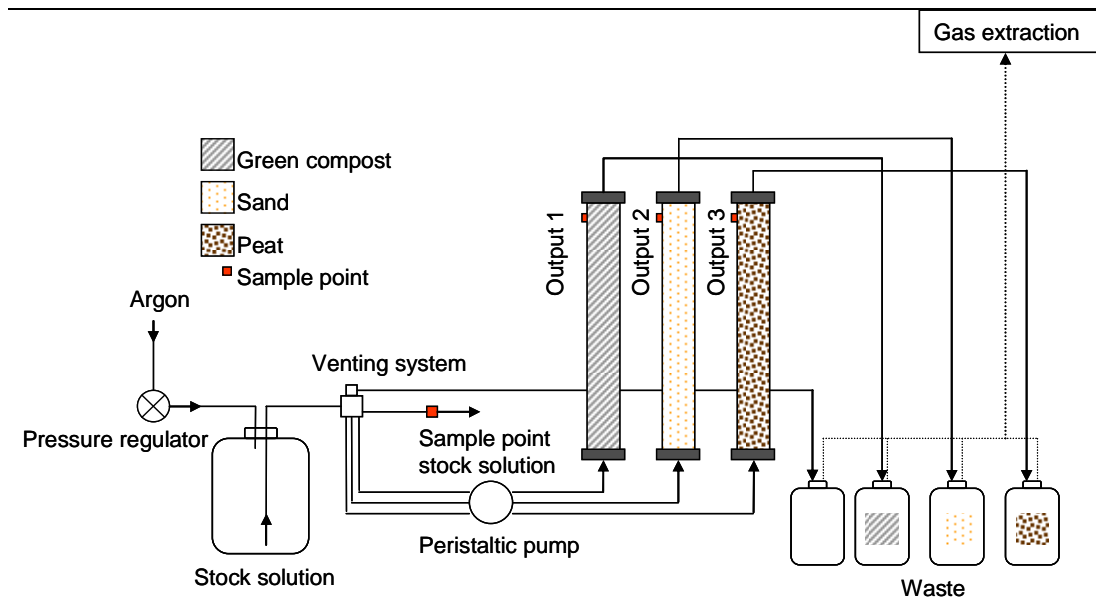
## 5

Recommendations for future column experiments





During the column experiments some design limitations of the columns became clear. These design limitations made it hard to control the working of the columns. Some design and control recommendations will be done here for future column experiments (fig. 0.1).



**Figure 0.1 recommended column set-up for future column experiments.**

Improvements and points of attention:

1. Sample points directly in the column: in this way there will be no losses due to sorption at the viton tubes. Furthermore, no contamination due to previous sampling will occur. In short, it is a cleaner and better way of sampling. Make sure that sampling is done at the same speed as the discharge of the column.
2. Fill the columns with material and water at the same time, and weigh the material while doing this. This ensures that no oxygen is included in the columns.
3. Every column its own waste barrel: this enhances the controllability of the experiment, because the average discharge of each column can be checked. The waste barrels could even be placed on top of a scale, which is connected to a plotter. This could be used to control the discharge in time. Furthermore, different waste lines also prevent interaction and influences between the columns.
4. Glass foam instead of glass pearls: the glass pearls which are used in this experiment are quit thin and did not prevent clogging by the relatively small particle size of the peat. Some sort of foam could be a better filter.
5. Three pumps: this could be an option when the discharge has to be equal, but it failed to do this with one pump.
6. Pump check: the stock solution has been put under pressure, which also ensures that the pump is under pressure. The pump will determine the discharge to the columns. When, however, a peristaltic pump is not properly installed the discharge could be influenced by the pressure on the stock solution.



# Appendix

## 6

Contaminant database for  $K_{oc}$  and degradation



Stof en brutoformule	ref	Dichtheid (kg/l)	S (ca 20°C) (mg/l)*	log Koc (l/kg)**	log Kom (l/kg)***	R****	biologische afbraak in bodem					Microbiële toxiciteit
							aerob	anaerob				
								nitraatred.	ijzerreduc.	sulfaatred.	methanog.	
benzeen C6H6	1	-	1.780	1,9	1,66	1,7 - 2,7	-	-	-	-	-	EC <sub>50</sub> = 92 mg/l
	2	0,87	1.780	1,9-2,0	1,65-1,80		-	-	-	-	-	
	3 <sup>3)</sup>	0,88	1.780	1,7	1,42		2,5*10 <sup>-2</sup> d <sup>-1</sup>	-	-	-	3,7*10 <sup>-3</sup> d <sup>-1</sup>	
	4 <sup>3)</sup>	0,88	1.735	1,8	1,52		-	-	-	-	-	
	5	-	1.780	1,9	1,62		-	-	-	-	-	
	6	0,88	1.780	-	-		-	-	-	-	-	
	7 <sup>3)</sup>	-	-	-	-		0,29 d <sup>-1</sup>	-	-	-	4,3*10 <sup>-3</sup> d <sup>-1</sup>	
	10	-	-	-	-		0,007 d <sup>-1</sup>	nihil - 4*10 <sup>-3</sup> d <sup>-1</sup>	2,1*10 <sup>-4</sup> d <sup>-1</sup>	-	nihil - 4,9*10 <sup>-3</sup> d <sup>-1</sup>	
	11	-	-	-	-		-	-	1,2*10 <sup>-2</sup> d <sup>-1</sup>	-	-	
	15	-	-	-	-		-	0,006 - 0,0014 d <sup>-1</sup>	-	-	-	
	18	-	-	-	-		-	-	-	-	4,3*10 <sup>-3</sup> d <sup>-1</sup>	
	19	-	-	-	-		-	-	-	nihil - 6,1*10 <sup>-2</sup> d <sup>-1</sup>	-	
	20	-	-	-	-		-	-	-	-	1,2*10 <sup>-2</sup> d <sup>-1</sup>	
	22 <sup>3)</sup>	-	-	-	-		-	0,335 d <sup>-1</sup>	0,008 d <sup>-1</sup>	0,009 d <sup>-1</sup>	0,008 d <sup>-1</sup>	
32	-	-	-	-	-	overall 9,5*10 <sup>-4</sup> - 9,5*10 <sup>-2</sup> d <sup>-1</sup>						
tolueen C7H8	1	-	515	2,10	1,86	2,9 - 5,9	-	-	-	-	-	-
	2	0,87	515	3,45-3,9	2,0-2,26		-	-	-	-	-	
	3 <sup>3)</sup>	0,87	515	2,13	1,89		-	-	-	-	-	
	4 <sup>3)</sup>	0,86	615	2,11	1,87		-	-	-	-	-	
	6	0,87	515	-	-		-	-	-	-	-	
ethylbenzeen C8H10	1	-	152	2,20	1,96	3,4 - 9,2	-	-	-	-	-	-
	2	-	152	-	-		-	-	-	-	-	
	3 <sup>3)</sup>	0,87	152	-	-		-	-	-	-	-	
	4 <sup>3)</sup>	0,86	178	2,37	2,13		-	-	-	-	-	
	5	-	140	2,73	2,49		-	-	-	-	-	
naftaleen C10H8	1	-	30	3,00	2,76	13,2 - 20	-	-	-	-	-	-
	2	-	32	-	-		-	-	-	-	-	
	3 <sup>3)</sup>	1,15	30	2,90	2,66		-	-	-	-	-	
	4 <sup>3)</sup>	1,04	30	3,1	2,86		-	-	-	-	-	
	5	-	31	3,1	2,86		-	-	-	-	-	
o-xyleen C8H10	1	-	-	-	-	3,7 - 7,1	-	-	-	-	-	-
	2	0,87	175	2,53-2,59	2,29-2,36		-	-	-	-	-	
	3 <sup>3)</sup>	0,88	175	2,57	2,33		-	-	-	-	-	
	4 <sup>3)</sup>	0,88	164	2,24	2,00		-	-	-	-	-	
	6	0,88	175	-	-		0,20 d <sup>-1</sup>	-	-	-	5,5*10 <sup>-3</sup> d <sup>-1</sup>	
	7 <sup>3)</sup>	-	-	-	-		9,2*10 <sup>-3</sup> d <sup>-1</sup>	-	4,1*10 <sup>-3</sup> d <sup>-1</sup>	-	-	
	15	-	-	-	-		-	1,2*10 <sup>-3</sup> d <sup>-1</sup>	-	-	-	
	22 <sup>3)</sup>	-	-	-	-		0,035 d <sup>-1</sup>	0,005 d <sup>-1</sup>	0,002 d <sup>-1</sup>	0,011 d <sup>-1</sup>	0,001 d <sup>-1</sup>	
33	-	-	-	-	0,029 d <sup>-1</sup>	-	-	-	-			
m-en p-xyleen C8H10	1	-	180	2,6	2,36	5,9 - 13,8	-	-	-	-	-	-
	2	0,87	198	2,50-2,92	2,26-2,66		-	-	-	-	-	
	3 <sup>3)</sup>	0,86	198	2,92	2,66		-	-	-	-	-	
	4 <sup>3)</sup>	0,86	197	2,82	2,58		-	-	-	-	-	
	6	0,86	198	-	-		5,7*10 <sup>-2</sup> d <sup>-1</sup>	-	-	-	-	
	7 <sup>3)</sup>	-	-	-	-		1,3*10 <sup>-2</sup> d <sup>-1</sup>	-	2,7*10 <sup>-3</sup> d <sup>-1</sup>	-	-	
	15	-	-	-	-		-	2,4*10 <sup>-3</sup> d <sup>-1</sup>	-	-	-	
	22 <sup>3)</sup>	-	-	-	-		0,107 d <sup>-1</sup>	0,013 d <sup>-1</sup>	0,002 d <sup>-1</sup>	0,033 d <sup>-1</sup>	0,002 d <sup>-1</sup>	
33	-	-	-	-	0,029 d <sup>-1</sup>	-	-	-	-			
n-hexaan (C6) C6H14	1	-	-	2,9	2,66	13,2	-	-	-	-	-	-
	3 <sup>3)</sup>	0,66	13	-	-		-	-	overall 0,08 d <sup>-1</sup>	-	-	
	4 <sup>3)</sup>	0,66	12,3	-	-		-	-	-	-	-	
	21 <sup>3)</sup>	-	-	-	-		0,18 - 2,5 d <sup>-1</sup>	-	-	-	-	
n-octaan (C8) C8H18	1	-	-	3,6	3,36	62	-	-	-	-	-	-
	3 <sup>3)</sup>	0,7	0,66	-	-		-	-	overall 0,097 d <sup>-1</sup>	-	-	
	4 <sup>3)</sup>	0,7	0,76	-	-		-	-	-	-	-	
	21 <sup>3)</sup>	-	-	-	-		0,18 - 2,5 d <sup>-1</sup>	-	-	-	-	



