A modelling study on the efficiency of groundwater treatment walls in heterogeneous aquifers

M. FINKEL, R. LIEDL & G. TEUTSCH

Department of Applied Geology, University of Tübingen, Sigwartstrasse 10, D-72076 Tübingen, Germany

Abstract The heterogeneity of hydraulic and physico-chemical aquifer properties leads to a non-uniform spatial and temporal distribution of the groundwater velocity and the contaminant concentration at the inlet of treatment walls (gates) within funnel-and-gate systems. These variations of the contaminant mass flux may have a large impact on the efficiency of these systems. This study focuses on the migration and immobilization of polycyclic aromatic hydrocarbons (PAH) within a treatment wall (reactor) consisting of granular activated carbon (GAC). Three different GACs are considered as treatment materials. The modelling tool SMART (Streamtube Model for Advective and Reactive Transport) is applied to assess the impact and relative importance of the most relevant parameters. It is found that the PAH transport through GAC can be modelled by assuming non-equilibrium sorption conditions and that the impact of the parameters depends on how close the treatment system is to equilibrium.

INTRODUCTION

The clean-up of soil and groundwater contaminated by not readily soluble chemicals, such as PAH, by conventional pump-and-treat technologies has led to unsatisfactory results in many cases (e.g. Mackay & Cherry, 1989; Travis & Doty, 1990). Passive remediation technologies, such as funnel-and-gate systems, have been suggested as promising alternatives to achieve more efficient clean-up strategies at a lower financial effort (e.g. Gillham & O'Hannesin, 1992; Starr & Cherry, 1994). However, hydraulic and physico-chemical aquifer heterogeneities are known to have a large impact on reactive solute transport (e.g. Sudicky, 1986; Mackay et al., 1986; Barber II et al., 1992; Grathwohl & Kleineidam, 1995). Thus, even if constant dissolution rates from the contaminant source could be assumed, the heterogeneous nature of the aquifer upstream of a funnel-and-gate system leads to a spatially and temporally non-uniform distribution of the contaminant mass flux at the inlet of the treatment wall (reactor). These variations have to be taken into account when funnel-and-gate systems are to be designed.

Granular activated carbon (GAC) is recognized as a very strongly sorbing porous medium extensively used in wastewater treatment. Due to its high sorption capacity and intergranular porosity GAC is a particularly suitable material for permeable barriers. For PAH sorption onto GAC extremely high sorption capacities were observed (e.g. Walters & Luthy, 1984). However, Grathwohl & Peschik (1997) found in laboratory column studies that the observed retardation factors are much lower than retardation factors calculated by assuming equilibrium conditions. They could interpret their observation using a diffusion-limited sorption process and Peschik (1997) showed that the measured sorption uptake in a close batch system...
agree very well with model results based on Fick's second law for intra-particle diffusion.

In order to gain a better understanding of the processes in operation, as well as of the relative importance of the relevant parameters, the modelling tool SMART (Streamtube Model for Advevtive and Reactive Transport) for simulating three-dimensional transport in hydraulically and physico-chemically heterogeneous aquifers has been developed (Finkel et al., 1997a). In this study SMART is applied to the transport of selected PAH in treatment walls consisting of GAC. Based on experimentally measured input parameters (Grathwohl & Peschik, 1997; Peschik, 1997) PAH breakthrough curves are calculated. Further parameter studies are carried out in order to estimate the sensitivity of the PAH residence time on the relevant parameters.

**MATHEMATICAL TRANSPORT MODEL**

SMART is based upon a Lagrangian streamtube concept for modelling reactive solute transport in heterogeneous porous aquifers (Dagan & Cvetkovic, 1996). According to this concept, conservative transport and reactive processes can be treated separately. Conservative transport is quantified with respect to the travel time $\tau$ of an inert tracer, resulting in a probability density function (pdf) $g(\tau,x)$ of travel times for non-reactive solutes between an injection and a control surface (Fig. 1). The pdf represents the impact of hydraulic aquifer heterogeneity on solute transport. The
function $g$ may be either measured (tracer experiment) or determined by applying analytical or numerical models.

Reactive transport is also described with respect to the travel time $\tau$ of inert solutes leading to a reaction function $I(\tau, t)$. For any fixed time $t$ this function represents a normalized concentration profile referring to all positions within the streamtubes that have been reached by a conservative tracer after a travel time $\tau$. $I$ is evaluated by simulating the one-dimensional reactive transport with respect to $\tau$. The transport model accounts for any type of equilibrium reactions as well as for mass-transfer limited sorption which is modelled by an intra-particle diffusion approach (Finkel & Liedl, 1997). By multiplying $g$ by $I$ with respect to $\tau$, mean arrival times and mean breakthrough curves for reactive solutes are obtained. For further details about SMART see Finkel et al. (1997a,b).

MODELLING SCENARIO AND INPUT PARAMETERS

In modelling a funnel-and-gate system, one has to deal with two transport media, the natural aquifer material and the artificial reactor (gate) filling. Due to their significantly different hydraulic and physico-chemical properties a zonation of the modelling area is introduced (Fig. 2). In this paper the PAH transport through the gate (zone B) is considered. Given a pure and homogeneous GAC filling with a relatively narrow grain size range, it is reasonable to assume that approximately parallel flow conditions prevail in the gate. Consequently the only streamtube associated with the most unfavourable boundary conditions at the gate inlet, i.e. high flow velocities and contaminant concentrations, will be critical concerning the time span that the contaminant emission at the reactor outlet is kept below the target value (concentration limit). Therefore, one-dimensional simulations should be sufficient when estimating efficiency criteria for the use of GAC reactors within the framework of a funnel-and-gate system. In the following numerical simulations the same PAHs (acenaphthene (ACE), fluorene (FLN), and phenanthrene (PHE)) and GACs (F100,
C 40/4, and TE 143) as used in the work of Grathwohl & Peschik (1997) and Peschik (1997) have been considered.

The measured sorption isotherm parameters provided by Grathwohl & Peschik (1997) are summarized in Table 1. The measured intra-particle and filter porosity are 35% and 52% (F 100), 44% and 62% (C 40/4), and 40% and 50% (TE 143, estimated). Furthermore, it is assumed that the maximum aqueous concentrations of the PAHs equal their aqueous solubilities $C_{\text{sat}, \text{mix}}$ in equilibrium with a coal tar phase. Values of $C_{\text{sat}, \text{mix}}$ for ACE, FLN and ACE, as measured by Merkel (1996), are listed in Table 1. Further parameters which are subject to variation within the parameter studies are assumed as follows: grain size diameter $d = 1$ mm, average groundwater pore velocity in the considered streamtube $v = 5 \times 10^{-5}$ m s$^{-1}$ and thickness of the treatment wall (gate) $L = 0.5$ m. The remediation target has been taken from the regulations of the State of Baden-Wuerttemberg, Germany, with a general PAH concentration limit of 0.15 $\mu$g l$^{-1}$.

### Table 1 Freundlich isotherm parameters and aqueous solubilities $C_{\text{sat}, \text{mix}}$.

<table>
<thead>
<tr>
<th>Type of GAC</th>
<th>Acenaphthene: $C_{\text{sat}, \text{mix}}$ (µg l$^{-1}$): 30</th>
<th>Fluorene: $C_{\text{sat}, \text{mix}}$ (µg l$^{-1}$): 100</th>
<th>Phenanthrene: $C_{\text{sat}, \text{mix}}$ (µg l$^{-1}$): 180</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\log K_f$ (kg l$^{-1}$) $n_f$ $D_{\text{app}}$ (cm$^2$ s$^{-1}$)</td>
<td>$\log K_f$ (kg l$^{-1}$) $n_f$ $D_{\text{app}}$ (cm$^2$ s$^{-1}$)</td>
<td>$\log K_f$ (kg l$^{-1}$) $n_f$ $D_{\text{app}}$ (cm$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>F 100</td>
<td>6.2 0.59 6.0e-13</td>
<td>6.1 0.81 5.2e-13</td>
<td>5.9 0.56 3.8e-12</td>
</tr>
<tr>
<td>C 40/4</td>
<td>6.0 0.87 1.2e-12</td>
<td>5.9 0.99 1.7e-13</td>
<td>5.7 0.70 9.6e-12</td>
</tr>
<tr>
<td>TE 143</td>
<td>5.2 0.92 1.0e-11*</td>
<td>5.6 0.67 1.0e-11*</td>
<td>5.7 0.56 1.0e-11*</td>
</tr>
</tbody>
</table>

* estimated

### RESULTS

#### PAH breakthrough curves

First, the one-dimensional non-equilibrium transport of the PAHs ACE, FLN and PHE through the GACs F 100, C 40/4 and TE 143 was modelled. Breakthrough curves (BTCs) were calculated for input concentration of 10% and 100% of $C_{\text{sat}, \text{mix}}$ of the respective PAH. Figure 3 reveals that:

(a) a lower input concentration leads to a later breakthrough which is expected given the nonlinearity of the sorption isotherms;

(b) the time scale of PAH breakthrough in the GACs varies considerably;

(c) the residence times of the ACE, FLN and PHE are very different, although only three-ring components with similar properties are considered. Given (a), these differences can be explained by the different values of $C_{\text{sat}, \text{mix}}$ (Table 1).

#### Parameter studies

In order to assess the relative importance on the PAH residence time $T$ (before the concentration limit is reached) in the GAC treatment wall, a series of simulations...
have been conducted varying $L/v$, $d$ and the apparent diffusion coefficient, $D_{app}$, starting from the reference values given in the previous section (10% of $C_{sat,mix}$). As shown in Fig. 4, $T$ is strongly affected by variations of the residence time $L/v$ of a conservative tracer. For high values of $L/v$ the PAH breakthrough can be predicted by assuming equilibrium conditions. For lower values an additional non-equilibrium effect appears to occur which is indicated by an increasing slope (Fig. 4). Figure 5 reveals that, up to a certain GAC grain diameter $d$ between 0.1 and 1 mm, there is almost no effect on $T$ at all. Here, small diameters lead to a “fast” sorption and near-equilibrium conditions. For larger grain diameters, a linear decrease in $T$ with respect to $d$ on the log-log plot can be observed. Figure 6 shows a slightly weaker dependency of $T$ on the apparent diffusion coefficient $D_{app}$ with a decreasing effect for increasing values of $D_{app}$. The decreasing influence of lower values of $d$ and of higher values of $D_{app}$ can be explained by sorption kinetics gradually approaching equilibrium conditions.

CONCLUSIONS

This study offers evidence that PAH migration through GAC treatment walls has to be simulated under non-equilibrium conditions. It has been shown that the extent of the influence of all the parameters considered here depends on how close the system is to equilibrium conditions. Furthermore, in view of the very different time scales achieved for PAH breakthrough in the GACs used in this study, the choice of the
Dependence of breakthrough time $T$ of ACE (a), FLN (b) and PHE (c) on the conservative residence time $L/v$.

![Graph](image)

**Fig. 4** Dependency of PAH residence time $T$ on $L/v$: (a) ACE, (b) FLN, (c) PHE.

Dependence of breakthrough time $T$ of ACE (a), FLN (b) and PHE (c) on the GAC diameter $d$.

![Graph](image)

**Fig. 5** Dependency of PAH residence time $T$ on GAC diameter $d$: (a) ACE, (b) FLN, (c) PHE.
appropriate GAC may be one of the key issues when designing a treatment system. Further investigations concerning both the contaminant transport upstream of the reactor and the PAH sorption onto the GAC should be carried out to narrow the range of possible parameter variations.

REFERENCES


Mackay, D. M., Ball, W. P. & Durant, M. G. (1986) Variability of aquifer sorption properties in a field experiment on


