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Removal of Volatile Organic Compounds in Vertical Flow Filters: Predictions from Reactive Transport Modeling

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Abstract

Vertical flow filters are containers filled with porous medium that are recharged from top and drained at the bottom, and are operated at partly saturated conditions. They have recently been suggested as treatment technology for groundwater containing volatile organic compounds (VOCs). Numerical reactive transport simulations were performed to investigate the relevance of different filter operation modes on biodegradation and/or volatilization of the contaminants and to evaluate the potential limitation of such remediation mean due to volatile emissions. On the basis of the data from a pilot-scale vertical flow filter intermittently fed with domestic waste water, model predictions on the system's performance for the treatment of contaminated groundwater were derived. These simulations considered the transport and aerobic degradation of ammonium and two VOCs, benzene and methyl tertiary butyl ether (MTBE). In addition, the advective-diffusive gas-phase transport of volatile compounds as well as oxygen was simulated. Model predictions addressed the influence of depth and frequency of the intermittent groundwater injection, degradation rate kinetics, and the composition of the filter material. Simulation results show that for unfavorable operation conditions significant VOC emissions have to be considered and that operation modes limiting VOC emissions may limit aerobic biodegradation. However, a suitable combination of injection depth and composition of the filter material does facilitate high biodegradation rates while only little VOC emissions take place. Using such optimized operation modes would allow using vertical flow filter systems as remediation technology suitable for groundwater contaminated with volatile compounds.

Introduction

Vertical flow filters reproduce the mechanisms of vertical water flux and transport of natural soil and subsoil under a controlled environment for contaminant degradation, which at a pilot scale allows for the study of processes and test of efficiency of such systems. If they are planted they are called vertical flow constructed wetlands, and represent artificial emulators of natural wetlands. First applications of constructed wetlands date back to the beginning of the 20th century (Vymazal 2011), although first considered as water remediation technique in the 1970s (Seidel 1973). Since then the vertical filter systems have most commonly been used for the treatment of domestic waste water as they provide a highly efficient, simple and easy to operate, low maintenance, and decentralized technology. Over the years, the use of constructed wetlands in general has been extended world wide not only for domestic waste water treatment, but also for the treatment of other types of waste water generated from different sources as, for example, from agriculture, mining, pharmacy as well as petroleum industry (Knight et al. 1998, 1999; Ji et al. 2002; Keefe et al. 2004; Langergraber and Šimunek 2005; Wallace and Kadlec 2005; Eke and Scholz 2008; Kadlec and Wallace 2008; Langergraber 2008; Vymazal 2011).

Recently, constructed wetland technologies (including vertical flow systems) have been proposed also for the treatment of groundwater containing volatile organic contaminants (e.g., benzene and methyl tertiary butyl ether [MTBE]; Rügner et al. 2007). However, high volatility can cause unwanted atmospheric emissions associated with adverse environmental or health risks. This compromises the applicability of this treatment technology for such compounds. Volatile organic compound (VOC) emissions from contaminated groundwater and transport through the unsaturated zone have been studied over the last decades (Pasteris et al. 2002; Rivett et al. 2011). Owing to VOC-related health concerns, environmental policies set up regulation and treatment techniques to avoid and deal with VOC emissions (European Commission Environment 2011; USEPA 2011).

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Another problematic aspect is monitoring of remedial performance. Standard practice for the assessment of filter contaminant removal performance compares dissolved concentration measurements from inflow and outflow of the wetland. However, this is not sufficient for the distinction between the effects of removal of volatile compounds by biodegradation (desired process) and/or by volatilization (undesired process). Experimental studies on the emission of volatile compounds from vertical flow filters are missing so far, which is not surprising as the measurement of emitted fluxes of gaseous compounds at field conditions is a challenge. Still, knowledge of the factors that control the volatile emissions of contaminants is specifically needed for optimal filter design. A primary design criterion is to obtain good connectivity between unsaturated soil and atmosphere which is necessary to continuously provide oxygen. High connectivity means high oxygen availability, but it simultaneously promotes the transfer of volatilized contaminants to the atmosphere.

In spite of their simplicity, vertical flow filters exhibit a complex behavior in terms of water flow, the transport of dissolved and gaseous species, as well as phase exchange processes and the biotic and abiotic reactions affecting the fate of contaminants. The performance of such filters is routinely evaluated as a black box, without a detailed and quantitative consideration of the governing processes that control the performance of the system. One way to obtain more insight is the use of numerical model simulations. Models offer the opportunity to simulate the performance of given systems. They allow computing in detail flow dynamics and solute transport, while they facilitate differentiation of the role of individual processes and system parameters (Schwager and Boller 1997; Langergraber 2001; Keefe et al. 2004). Furthermore, they are inexpensive means for scenario analysis, and allow testing of different technical system configurations and/or application strategies. This enables to elaborate on sensitive technological design criteria and to derive conclusions on optimal filter application. Recent studies on constructed wetland simulation demonstrated the benefit from attuned modeling concepts; for instance, simulation of reactive processes (Sklarz et al. 2010) as well as advective-diffusive transport of oxygen (Wanko et al. 2006; Forquet et al. 2009). Langergraber (2008) showed in his recent review that available reactive transport modeling concepts are sufficiently advanced for adequate simulation of vertical flow filters and the processes therein.

Applications of reactive transport models to vertical flow filters have so far focused on the fate of nonvolatile contaminants. The gas-phase processes considered in these models are restricted to those that control the release of oxygen to the water phase, and by this, for instance, the relevance of diffusive vs. advective gas-phase transport is discussed (Wanko et al. 2006). Our study uses numerical simulations considering simultaneously and at fully transient conditions unsaturated water flow, advective-dispersive transport of dissolved and of gaseous species as well as their reactive interactions. These numerical simulations were used to assess the removal of VOCs from a vertical flow filter, demonstrating how reactive transport modeling can also be employed for estimating VOC emissions from such treatment systems. In addition, our investigation showed that reactive transport modeling could be applied as a fast and inexpensive alternative for design and operation improvement of vertical flow filters preventing human and atmospheric risks caused by undesired VOC emissions.

The specific case selected was a filter system operated for the treatment of domestic waste water (Baeder-Bederski et al. 2004). The objective was to simulate the potential fate of benzene and MTBE, two volatile groundwater contaminants, and ammonium as nonvolatile contaminant, introduced by intermittent irrigation. By setting up different model variants the associated bioremediation performance of different vertical flow filter configurations and application strategies are predicted. Model results are used to assess the risk of atmospheric emissions and the influence of different operation modes on the magnitude of these emissions. The obtained results support the decision if and at which conditions vertical flow filters are a suitable treatment technology for contaminated groundwater and how to optimize their remediation performance for such compounds.

Materials and Methods

General Approach

A vertical flow filter from a domestic waste water treatment pilot plant located in Langenreichenbach, Germany (operating 14 different vertical and horizontal flow constructed wetlands) was used as a reference system for the behavior of such a filter at field conditions. This filter was used for the treatment of waste water containing nonvolatile compounds with ammonium as the main contaminant removed in the filter. Data on the flow rate and the concentration of ammonium at the inflow and outflow of this selected filter were gathered to set up and calibrate a numerical reactive transport model. The calibrated model was applied for the simulation of an analogous virtual system to be used for the treatment of contaminated groundwater. For this purpose, volatile compounds (benzene and MTBE) and associated abiotic processes (volatilization and gas-phase transport) were additionally considered in the model. The concentrations assumed for these two contaminants are characteristic for polluted groundwater found at an industrial site in Leuna, Germany. The model was used to predict the contribution of volatilization and biodegradation to the removal of the contaminants at different filter operation modes or under different filter design conditions.

Vertical Flow Filter Used as Field-Scale Experimental Reference

The reference filter had a rectangular surface area of 6.2 m^2 (2.4 m × 2.75 m, reduced by the presence of an outlet shaft of 0.4 m^2), and was planted with *Phragmites australis.* The filter matrix consisted of layered granular material of different diameters: a 5-cm-thick coarse fluvial gravel cover layer (8 to 16 mm diameter) on top, a 60-cm-thick main layer composed by a mixture of 30% crashed expanded clay pellets (2 to 4 mm) and 70% sand (2 mm), and a 10-cm-thick gravel drainage layer (4 to 8 mm) separated by a perforated stainless steel plate (2-mm-diameter holes) from a 20-cm-thick sump at the bottom (Figure 1). The filter was

Figure 1. Vertical flow filter schematic cross section—the arrow indicates the injection depth of Scenario 2 (base case).

intermittently loaded by pulses of water via two perforated pipes located on top of the filter. The total water volume injected per day was 248 L, applied every 6 h in individual pulses with rates of 20 L/min and 3.1 min duration. Flow rates measured at the inflow and outflow were used by Maier et al. (2009) to calibrate a numerical flow model of this filter and to determine the hydraulic properties of the filter material (van Genuchten coefficients, porosity, and saturated hydraulic conductivity of each filter layer). Maier et al. (2009) also provide a more detailed description of the material used for the vertical filter construction, and they give comprehensive insight in the operation of the water treatment pilot plant.

The vertical flow filter was in operation for about 2 years (2005 to 2006). Performance of the filter was monitored by approximately weekly sampling of the inflow and outflow water, and by the analysis of default chemical and biological parameters. Analytical methods and further details on measurement practice of water samples are provided by Baeder-Bederski et al. (2004). For the main contaminant, ammonium, results of this analysis indicated a stable filter performance of the entire year 2006. For this study, average ammonium concentrations of 88 mg/L at the inflow and 0.87 mg/L at the outflow for a regularly measured 2-month operation period (July to August 2006) were adopted as reference data (Table 1).

Numerical Model Set Up

Numerical simulations were carried out with the multicomponent reactive transport model MIN3P (Mayer et al. 2002), which is suitable for the simulation of variably saturated porous media systems. In addition to water flow and reactive transport of dissolved species in the water phase, the MIN3P version considered in this study allows also for simulating the diffusion and advective transport of gaseous species in the soil (Molins and Mayer 2007). The exchange of volatile species between gaseous phase and water phase (i.e., soil air and pore water) was simulated assuming an instantaneous local equilibrium between dissolved and gaseous concentrations as given by Henry's law.

Soil filters were simulated as one-dimensional vertical structures using a constant spatial discretization of 1 cm. For each simulated scenario, the intermittent irrigation pattern and chemical species concentrations in the injected water were assumed to be constant. Default atmospheric conditions (e.g., partial pressure of oxygen and nitrogen) were defined as boundary condition for the gas phase at the top of the filter. Transient simulations were performed until flow rates and concentrations had reached a repetitive daily pattern for at least twice the hydraulic residence time of the solute in the filter (determined by simulated tracer tests, see Table 2) to assure the result representing "steady" operation conditions.

Unsaturated Flow

MIN3P applies Richards equation to describe flow under unsaturated conditions. Hydraulic properties (hydraulic conductivities, van Genuchten parameters) of the materials used in the experimental reference vertical flow filter determined by automatic calibration were taken from Maier et al. (2009) and are listed in Table 1. With these parameter settings, the experimental results could be reproduced (Figure 2) as in the study by Maier et al. (2009).

The hydraulic residence time of water in the filters was determined by simulating a single-pulse injection of a nonreactive tracer (bromide). Tracer breakthrough at the outflow of the filter was taken to calculate residence times according to Headley and Kadlec (2007) (Table 2).

Reactive Processes

Three aerobic biodegradation processes were included in the model simulations: nitrification of ammonium, which for simplicity was implemented as one-step reaction (Prommer et al. 2006):

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + H_2O + 2\ H^+ \qquad (1)$$

and the total mineralization of benzene and MTBE (neglecting intermediate degradation products):

$$C_6H_6 + 7.5\ O_2 \rightarrow 6\ CO_2(g) + 3\ H_2O \qquad (2)$$

$$C_5H_{12}O + 7.5\ O_2 \rightarrow 5\ CO_2(g) + 6\ H_2O \qquad (3)$$

All degradation kinetics followed double Michaelis-Menten kinetics (Barry et al. 2002; Thullner et al. 2007):

$$\frac{\partial C_{\text{cont}}}{\partial t} = -k_{\max} \frac{C_{\text{cont}}}{k_{\text{cont}} + C_{\text{cont}}} \frac{C_{\text{o}_2}}{k_{\text{o}_2} + C_{\text{o}_2}} \qquad (4)$$

where C_{cont} is contaminant concentration, C_{o2} the oxygen concentration, $k_{\max}$ the maximum degradation rate, k_{cont}

Table 1

Parameter Values Used for Model Simulations

Settings	Unit	Value	Reference
Operation parameters			
Injection rate	L/min	20	Maier et al. (2009)
Duration of the pulse	min	3.1	”
Loading pulses per day	–	4	”
Volume of water injected per pulse	L	62	”
Volume of water injected per day	L	248	”
Loading distribution scheme	–	Uniform	”
Material properties			
Hydraulic conductivity$_{\text{clay+sand}}$	m/s	$7.01\ 10^{-7}$	”
Van Genuchten parameter (alpha)$_{\text{clay+sand}}$	1/m	0.76	”
Van Genuchten parameter (n)$_{\text{clay+sand}}$	–	2.7	”
Porosity$_{\text{clay+sand}}$	–	0.3969	”
Hydraulic conductivity$_{\text{gravel (8-16)}}$	m/s	$3.95\ 10^{-2}$	”
Van Genuchten parameter (alpha)$_{\text{gravel (8–16)}}$	1/m	3	”
Van Genuchten parameter (n)$_{\text{gravel (8–16)}}$	–	20.8	”
Porosity$_{\text{gravel (8–16)}}$	–	0.3045	”
Hydraulic conductivity$_{\text{gravel (4–8)}}$	m/s	$1.30\ 10^{-3}$	”
Van Genuchten parameter (alpha)$_{\text{gravel (4–8)}}$	1/m	8.5	”
Van Genuchten parameter (n)$_{\text{gravel (4–8)}}$	–	9.8	”
Porosity$_{\text{gravel (4–8)}}$	–	0.35	”
Residual saturation	–	0.01	”
Hydraulic conductivity $_{\text{sand}}$	m/s	$7.44\ 10^{-5}$	USEPA (2004)
Van Genuchten parameter (alpha)$_{\text{sand}}$	1/m	3.524	”
Van Genuchten parameter (n)$_{\text{sand}}$	–	3.177	”
Porosity$_{\text{sand}}$	–	0.3750	”
Residual saturation	–	0.053	”
Hydraulic conductivity $_{\text{building debris}}$	m/s	$5.4\ 10^{-5}$	Beyer et al. (2007)
Van Genuchten parameter (alpha)$_{\text{building debris}}$	1/m	154	”
Van Genuchten parameter (n)$_{\text{building debris}}$	–	1.29	”
Porosity$_{\text{building debris}}$	–	0.3100	”
Residual saturation	–	0.0	”
Lower boundary condition: fixed pressure head	m	–0.2	Maier et al. (2009)
Kinetics parameters			
Nitrification			
k_{max}	mg/L/s	$1.31\ 10^{-2}$	this study
k_{NH4+}	mg/L	$4.99\ 10^{-2}$	Langergraber and Šimunek (2005)
k_{O2}	mg/L	1.0	”
Benzene degradation			
k_{max}	mg/L/s	$1.56\ 10^{-3}$	Wendeberg (2010)
k_{C6H6}	mg/L	$7.8\ 10^{-1}$	Prommer et al. (1999)
k_{O2}	mg/L	$3.2\ 10^{-1}$	”
MTBE degradation			
k_{max}	mg/L/s	$1.76\ 10^{-4}$	Wendeberg (2010)
k_{C5H12O}	mg/L	$8.8\ 10^{1}$	Müller et al. (2007)
k_{O2}	mg/L	$3.2\ 10^{-1}$	Prommer et al. (1999)

Table 1 Continued

Settings	Unit	Value	Reference
Other reactive transport parameters			
Diffusion coefficient in aqueous phase	m^2/s	$6.105\ 10^{-10}$	USEPA (2010)
Diffusion coefficient in gas phase	m^2/s	$7.765\ 10^{-6}$	”
Longitudinal dispersivity	M	0.1	Giraldi et al. (2009)
Temperature	° C	10	Field measurement
Henry's law constant at 25 ° C			
Benzene	M/atm	$2.1\ 10^{-1}$	Robbins et al. (1993)
MTBE	M/atm	1.6	Dewulf et al. (1995)
Contaminants concentration			
NH_4^+ (experimental reference)	mg/L	87.5	Field measurement
NH_4^+ (prediction)	mg/L	60	Jechalke et al. (2010)
C_6H_6 (prediction)	mg/L	20	”
$C_5H_{12}O$ (prediction)	mg/L	4	”

the contaminant half saturation constant, and k_{o2} the oxygen half saturation constant. Values for the half saturation constants were taken either from literature or in the absence of literature sources, as for example, for the case of the oxygen half saturation constant for the MTBE degradation, it was assumed arbitrarily as the same oxygen half saturation constant used for the benzene degradation in the study by Prommer et al. (1999). Using these half saturation constants, values for the maximum degradation rates were determined by manually fitting measured data from the experimental reference (ammonium nitrification) or derived from laboratory experiments (benzene and MTBE from A. Wendeberg, personal communication, 2010). Table 1 provides an overview of all parameter values used. No further reactive processes (e.g., anaerobic degradation, acid base dissociations, mineral formation) were considered. Sorption processes were not considered assuming that for long-term operation of such filter systems sorptive retention is negligible. Furthermore, volatilization of nitrogen species was neglected. This is feasible because for the Langenreichenbach case measured pH was close to neutral and such volatilization could only take place in the form of NH_3 at alkaline pH (Burt et al. 1993) or in the form of nitrous acid at very acid pH (Buss et al. 2004). Additionally, the mass balance of nitrogen-compounds measured concentration values at the in- and outflow of the filter (not shown) does not suggest any volatile losses of nitrogen species.

Diffusive Processes

The MIN3P version employed in this study allows only for a single diffusion coefficient to be used for all species in each, the gaseous phase and the aqueous phase. Given that diffusion coefficients for oxygen differ from those for the organic contaminants, a decision was to be made on which value to select. Considering that the focus of the presented model simulation aims at the investigation of biodegradation and volatilization of benzene and MTBE, the average value of their diffusion coefficient in the air and in the water at 10 °C was used. Diffusion coefficients were obtained from the U.S. Environmental Protection Agency web page (USEPA 2010). The FSG (Fuller, Schettler, and Giddings), and Hayduck and Laudie methods (Lyman et al. 1990) were applied for temperature correction of the diffusion coefficient in air and water, respectively. Underlying equations and references are also presented in the mentioned web page. This simplification leads to a lower diffusion of oxygen in water and in air, but it avoids an overestimation of benzene and MTBE volatilization. Values used as average air and water diffusion coefficient are presented in Table 1. The longitudinal dispersivity presented in Table 1 was taken from a tracer test performed in vertical flow constructed wetlands (Giraldi et al. 2009), where vertical dimensions and particles diameter of the filter were similar to the systems simulated in this study.

Simulated Model Scenarios

The model setup calibrated for the experimental reference from Langenreichenbach served as a reference case to predict the performance of a vertical flow filter, with the same hydraulic characteristics, for the treatment of contaminated groundwater. The concentration of contaminants in the considered groundwater was taken from a contaminated site in Leuna, Germany, where ammonium, benzene, and MTBE are the main contaminants (Jechalke et al. 2010). Average contaminant concentrations are presented in Table 1.

To allow for longer residence times, the total length of the experimental reference system from Langenreichenbach was increased in the model simulations. This allows for enhanced biodegradation as long as oxygen is available. Further, the position of the infiltration system could be moved from the top of the filter down into the filter material while keeping a sufficient residual length of the flow path. The latter modification was aiming to mitigate volatile emissions of contaminants directly into the atmosphere.

The extended filters were composed of a 25-cm cover layer, a 120-cm main layer, and a 10-cm drainage layer using the same material properties as for the experimental reference. All simulated scenarios considered the same daily volume of injected water and the same contaminant

Table 2

Summary of Model Scenarios and Parameters – Volume of Injected Water per Day for All Scenarios: 248 L (40 L/m²)

Scenarios	Hydraulic Residence Time (d)	Injection Depth below Surface (m)	Pulses per Day	Duration of the Pulse (min)	Layers Specifications	Degradation Rate (mg/L/s)		
						Ammonium	Benzene	MTBE
1	11.3	On top	4	3.1	Main layer expanded clay and sand	$1.31\ 10^{-2}$	$1.56\ 10^{-3}$	$8.81\ 10^{-6}$
2[1]	11.7	0.30						
3[2]	11.7	0.30						
4	8.1	0.60						
5	6.5	0.90						
6	3.5	1.20						
7	11.8		1	12.4				
8	11.7		8	3.1				
9	11.7		16					
10	11.7		24					
11	11.5		Continuous injection					
12	11.7	0.30	4	3.1		13.14	1.56	$8.81\ 10^{-3}$
13	11.7					$1.31\ 10^{-5}$	$1.56\ 10^{-6}$	$8.81\ 10^{-9}$
14	11.7					no oxygen restriction		
15	4.4				Main layer sand	$1.31\ 10^{-2}$	$1.56\ 10^{-3}$	$8.81\ 10^{-6}$
16	7.7				Main layer building debris			
17	11.3				Cover layer 0.3 m			
18	8.5	0.60			Cover layer 0.6 m			
19	5.5	0.90			Cover layer 0.9 m			
20	3.1	1.20			Cover layer 1.2 m			

[1] model simulation taken as reference

[2] no gas advection considered

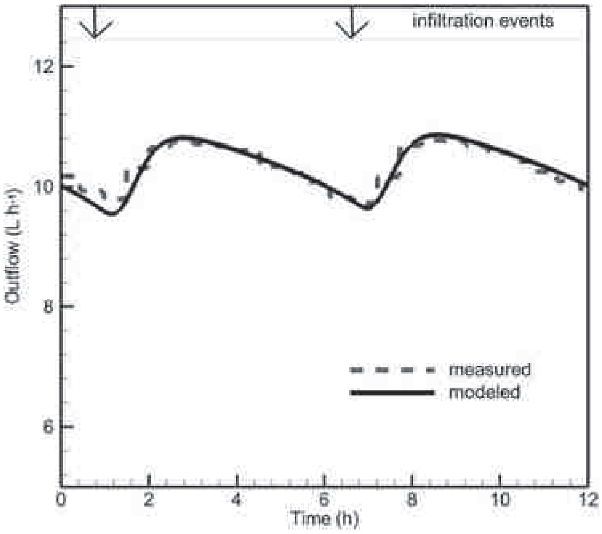

Figure 2. Comparison of calibrated flow model results (taken from Maier et al. 2009) and field data from the experimental reference system in Langenreichenbach.

concentrations in the injected water. In the simulations, water injection was distributed along a vertical zone of 5 cm thickness based on the field observation at Langenreichenbach, where at the moment of injection water application was not restricted to the injection point but to an area of 5 cm diameter. In different scenarios, the depth of injection (lower end of the 5-cm zone representing the location of the infiltration system) and the number of daily injection pulses were varied to test their influence on the performance of the filter system. To maintain a constant daily injected water volume, the duration of the pulse was modified while keeping injection rates constant. The only exception was the continuous injection scenario (Scenario 11), where the injection rate was modified to allow for a permanent injection while keeping the daily injected water volume constant.

Further scenarios addressed the influence of biodegradation kinetics (higher or lower maximum reaction rate, arbitrarily scaled by a factor of 1000 representing extreme cases each, and neglecting the oxygen dependency of the degradation rate kinetics in equation 4). Degradation rates of ammonium, benezene and MTBE have been extensively studied at the laboratory and the field scale (Burt et al. 1993; Suarez and Rifai 1999; Höhener et al. 2003, Schirmer et al. 2003; Buss et al. 2004; Eke 2008; Eke and Scholz 2008). Degradation rates are up to the order of 10^{-2}, 10^{-4}, and 10^{-7} mg/L/s for ammonium, benzene and MTBE respectively. Compared to these studies degradation rates used in this study are relatively high. However, as degradation rates have a strong dependence on the site-specific conditions, the site conditions of degradation rates obtained from the literature differ from the site conditions of the vertical flow filters considered here. The only case where systems are similar but not identical, since operation condition and the scale differs with the cases presented here, is in the case studied by Eke (2008), Eke and Scholz (2008).

Finally, the effect of different filter material configurations was examined. Either the thickness of the gravel cover layer was increased down to the top of the water injection zone, at the expense of the thickness of the main layer, or alternative materials (sand and building debris) were considered as main layer material. Hydraulic properties of these hypothetical material (Table 1) corresponded to a soil classified as sand according to the U.S. Soil Conservation System (SCS) (USEPA 2004) (soil type mainly composed by sand and/or gravel, with less than about 12% particles smaller than 0.075 mm in size) and to a recycled building material called RCB "recycling baustoff" (building debris), used as a noise barrier material (Beyer et al. 2007). It should be noted that the assumption of such filter material was made solely to gain a better insight in the processes occurring in the filter system and might not fulfill stability criteria required in practice.

An overview of all simulated scenarios is given in Table 2. In order to compare the different simulations, Scenario 2 (injection depth 30 cm; 4 injection pulses per day) was taken as base-case scenario. For each scenario, simulations were performed considering the nonreactive/abiotic (only transport and volatilization) and the reactive/biotic behavior (transport, volatilization, and biodegradation) of the contaminants. The role of volatilization was of special interest in all modeled scenarios. Therefore, model scenarios with and without advective transport of gaseous species were simulated. Model simulation result for the nongas advection cases is only shown for the base-case scenario.

All simulations were run until flow and reactive transport fluctuations reached a stable spatiotemporal pattern during a single infiltration cycle (e.g., period of time between two infiltration events). Model results were then analyzed for the temporal distribution of flow rates and chemical species fluxes at the in- and outflow and for the special distribution of water and chemical species at selected target times reflecting the dynamics of the system (first 5 min after injection: every minute; 5 to 15 min after injection: every 2 min; 15 to 30 min after injection: every 5 min; 30 to 60 minutes after injection: every 10 min; and then every hour until the next injection event). The simulated results were used to compute mass balances for each of the contaminants. Provided values for volatilization describe the fraction of contaminant mass that is emitted into the atmosphere via the top of the filter.

Results

Spatiotemporal Analysis of Two Example Scenarios

Two scenarios—the base-case Scenario 2 and Scenario 15, where the main layer is composed of sand—were selected to show the spatiotemporal variability of water saturation, oxygen, ammonium, and benzene concentrations along the filter profile (Figure 3). The shown vertical profiles represent the extreme values observed at each depth during a single cycle once stable patterns were achieved.

In Scenario 2, the main layer of the filter exhibits permanently high water saturations (more than 80%) with the upper 30 to 40 cm of the main layer temporarily reaching even full water saturation, while the cover and drainage layer presented water saturation of 10% or less. Constant oxygen concentration of about 11 mg/L was observed in the cover layer, while concentration decreased dramatically down to 0 mg/L at depths below 30 cm. Benzene and ammonium concentration profiles reflect this distribution of oxygen showing high variability only in the area above and around the injection depth with constant residual concentrations (and zero rates) at larger depths. A maximum concentration of 9.8 mg/L benzene, 3.45 mg/L MTBE (not shown), and 22.5 mg/L ammonium was observed at the injection depth. This is less than the applied groundwater concentrations and indicates a fast mixing between injected and residual water or a fast initial degradation. In the cover layer above the injection depth, a strong decrease of concentration was found for all contaminants: for ammonium a negligible concentration was reached at approximately 10 cm below the filter surface, while for benzene and MTBE this occurred only at the filter surface itself. Below the injection depth and down in the filter profile, concentrations remained constant at about 8.2 mg/L benzene, 3.4 mg/L MTBE (not shown), and 17.5 mg/L ammonium.

Results for Scenario 15 showed unsaturated conditions all over the entire filter profile. Highest water saturations were observed between 25 and 45 cm below the filter surface (up to 60% water saturation) and at the bottom of the filter main layer (90% water saturation). Cover layer and drainage layer exhibited water saturation of 10% or lower. A general decrease of oxygen concentration was observed along the filter profile, with concentrations of 11 mg/L on top of the filter and 9.6 mg/L at the bottom. Between 25 and 45 cm below the filter surface temporal variations were highest with smallest oxygen concentrations of 9.0 mg/L. Both benzene and ammonium concentration profiles exhibit pronounced concentration variations around and shortly below the injection depth with maximum values of 10.2 mg/L benzene and 32.5 mg/L ammonium, and negligible minimum values. In contrast, for MTBE (not shown) highest values of 3.5 mg/L were also found in the vicinity of the injection depths but concentrations showed only little variations with time. Maximum concentrations sharply decreased toward the top of the filter but only for ammonium nonnegligible values were found already below the top of the filter. Toward larger depths all contaminants showed a decrease of concentration reaching for ammonium and benzene negligible values already in the upper part of the main layer, while for MTBE (not shown) a concentration of 2.8 mg/L was still found at the bottom of the filter.

Hydraulic Residence Time

Simulated tracer breakthrough indicates a hydraulic residence time of 5.8 d for the pilot-scale vertical flow filter used as an experimental reference (not shown as a model scenario). When the filter length was extended the residence time increased to 11.3 d, for the same infiltration scheme (Scenario 1). For the other scenarios residence time varies mainly between 11 and 12 d, and decreased down to 3 d only for scenarios considering larger depths for the water injection (Table 2). As expected injection depth and residence

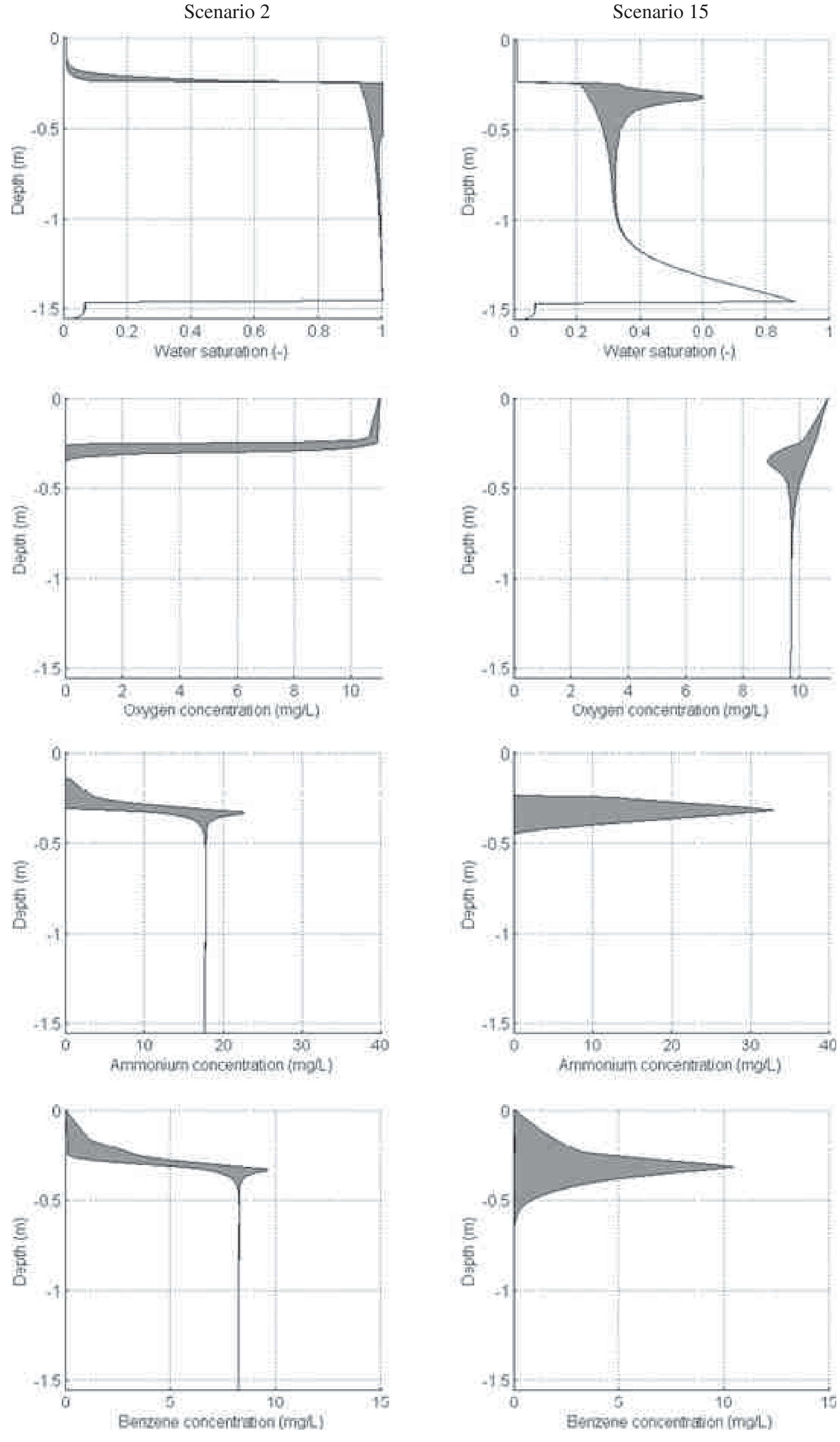

Figure 3. Simulation results for Scenario 2 (base case) and for Scenario 15 (main layer composed of sand). In each panel, shaded areas show ranges of temporal variations (maximum and minimum) during each injection cycle.

time exhibit a strong correlation ($R^2 = 0.91$) as the residence time is mainly controlled by the length of the travel path.

Abiotic Contaminant Removal

In the absence of biodegradation, volatilization would be the only removal process in the filter. Mass balances shown in Figure 4 thus represent the maximum volatilization potential for the considered filter system. For all scenarios the volatilization potential for benzene was larger than for MTBE reflecting their different volatilities. None of the scenarios yielded a complete volatilization of benzene and/or MTBE, but values of up to 66% for benzene and 23% for MTBE were found. These maximum values were obtained when injecting the contaminated water right on top of the vertical filters (Scenario 1). A reduction of the volatilization potential was reached when injecting water at increased depths (Scenarios 2 and 4 to 6). A high correlation of volatilization reduction with injection depth was observed for benzene and MTBE ($R^2 = 0.84$ and $R^2 = 0.91$, respectively). The temporal distribution of the injected water during each day was varied from 1 pulse to 24 pulses per day (Scenarios 2 and 7 to 11). Highest volatilization was found for four daily injection pulses (Scenario 2), but the variability of observed volatilization was rather small ranging between 27 and 37% for benzene and between 11 and 15% for MTBE. In contrast, for a continuous water injection, volatilization was reduced to less than 1% for benzene and for MTBE (Scenario 11).

When neglecting advective gas-phase transport (Scenario 3) the potential of volatilization remained the same as for the base-case scenario (Scenario 2). In comparison, the use of different filter materials had a much more significant effect. The use of building debris (Scenario 16) reduced volatilization for both contaminants while the use of sand (Scenario 15) enhanced it.

Abiotic and Biotic Removal

The observed contributions of the different removal processes (volatilization and biodegradation) were controlled by the volatility and degradability of the specific contaminants as well as by the availability of oxygen (Figure 5). The (biotic) removal dropped when injection depth was increased (Scenarios 1, 2, 4 to 6). The daily injection pattern exhibited highest removal when considering just a single injection pulse per day (Scenario 7). This fraction declined with higher injection frequencies (Scenarios 2 and 8 to 10), with minimum values reached for a continuous infiltration (Scenario 11).

As expected, increase or decrease of the maximum biodegradation rate (Scenarios 12 and 13) yields higher or lower removal, respectively, and full removal is achieved in case the biodegradation rate does not depend on the oxygen concentration in the filter (Scenario 14). Without advective gas-phase transport, contaminant removal is slightly reduced (Scenario 3). Changing the main filter

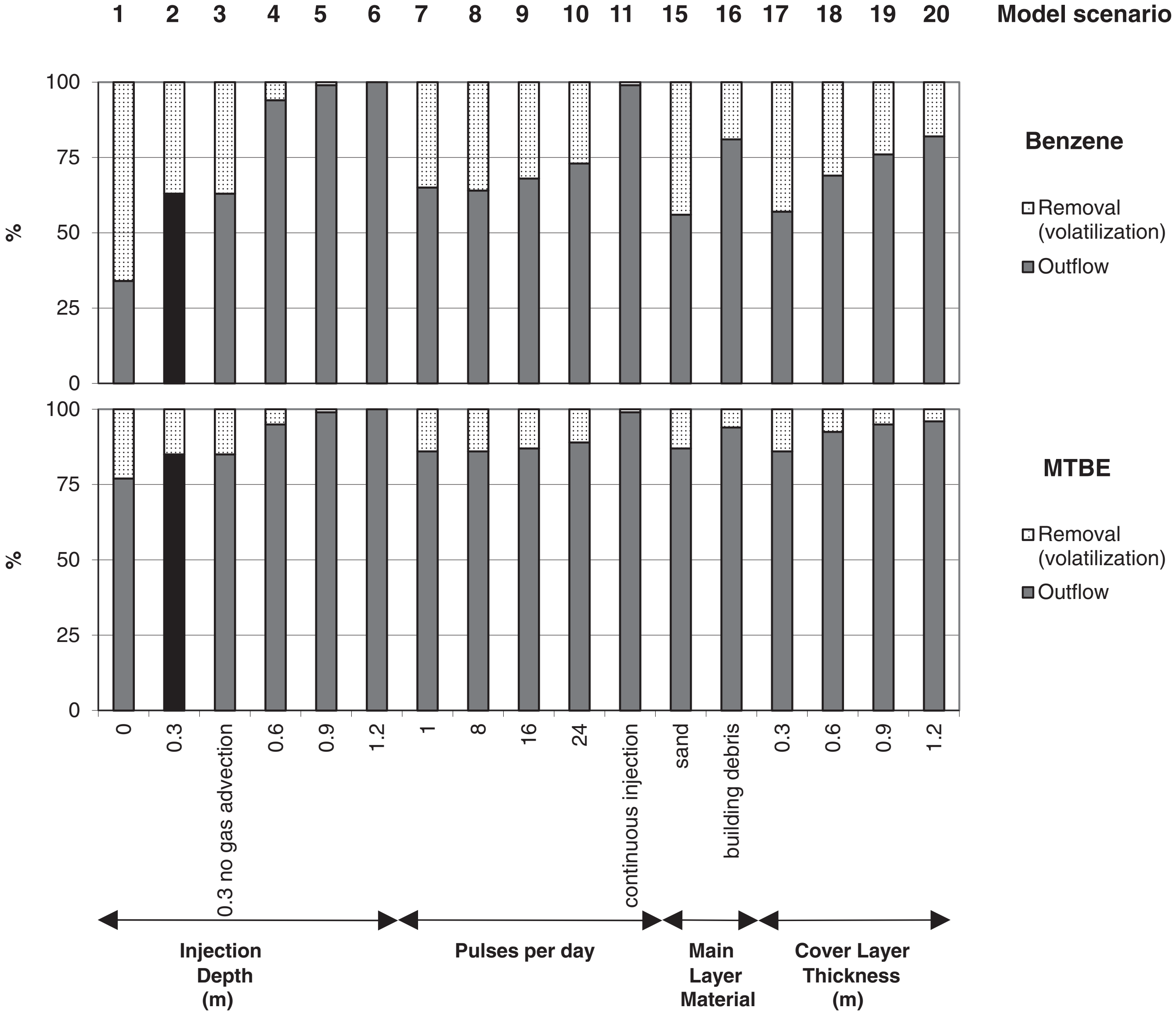

Figure 4. Mass balance of volatile contaminants (as the ratio of injected mass) in case of no biodegradation taking place in the vertical flow filter system. Scenario 2 (base case) is highlighted in black.

layer material to building debris (Scenario 16) reduces the contaminant removal, while sand (Scenario 15) results in a complete removal (except for MTBE). Also the use of thick cover layers reaching down to the injection depth raises removal for all tested depths (Scenarios 17 to 20 vs. Scenarios 2 and 4 to 6).

The contribution of volatilization and biodegradation to total removal of benzene and MTBE is shown in Figure 6. In all scenarios biodegradation is the main process contributing to the removal of benzene from the injected contaminated groundwater, with the only exception of Scenario 13, where very low degradation rate led to most of the benzene removed by volatilization. In turn, for most scenarios volatilization was the main MTBE removal process. However, biodegradation contribution to removal increased when biodegradation rates were increased (Scenario 12) or not limited by oxygen availability (Scenarios 14 and 15), or when the depth of injection avoided volatilization (Scenarios 5 and 6).

Oxygen Consumption

In most of the simulated scenarios oxygen concentrations at the outflow of the filter were far below 0.5 mg/L, which is given as upper limit for anoxic conditions (Wiedemeier et al. 1999). For most of these scenarios oxic conditions prevailed only in the upper part of the filter constrained by the injection depths (Figure 7). When water was applied at increasing injection depths or when the cover layer thickness

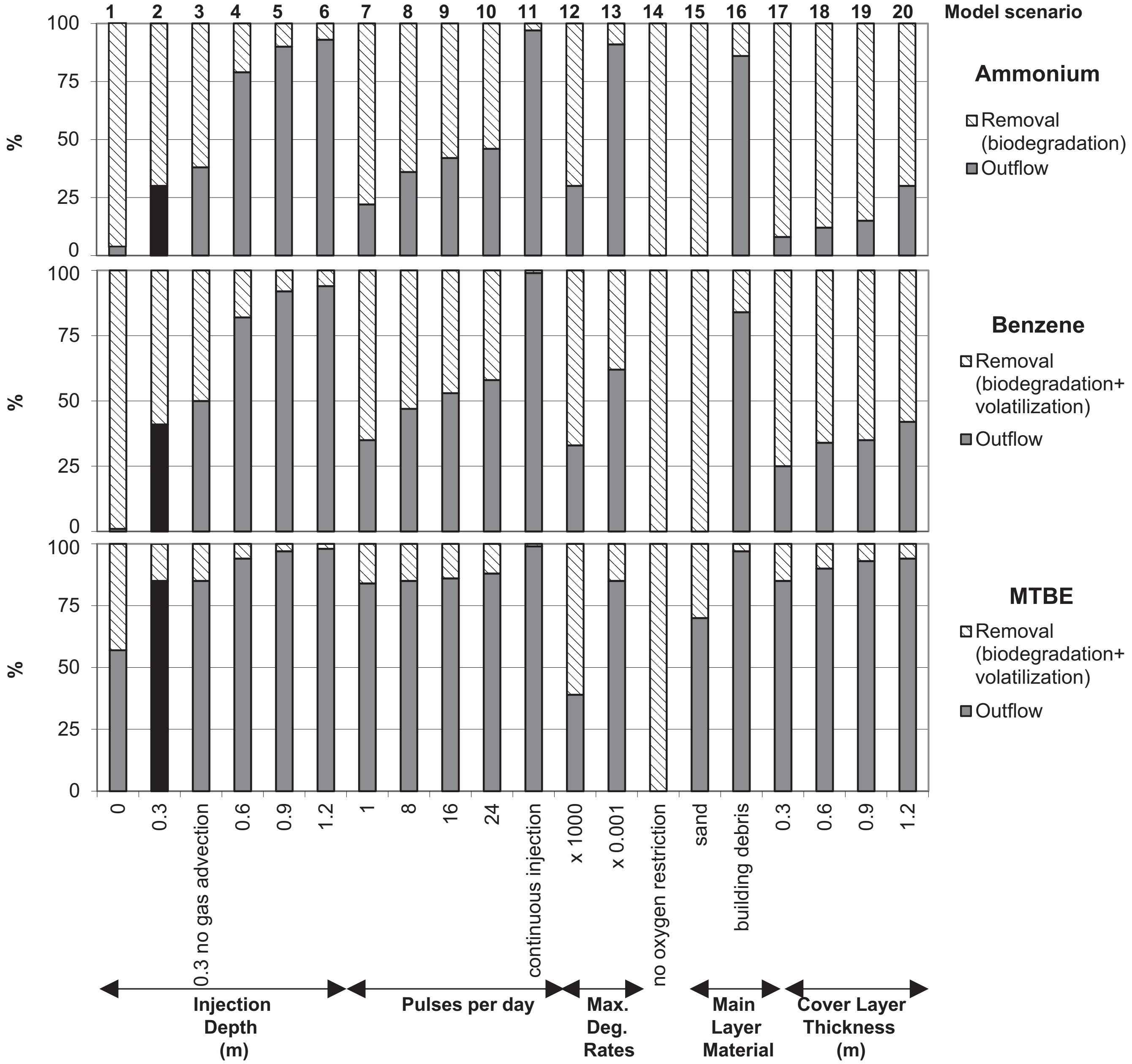

Figure 5. Mass balance of contaminants (as the ratio of injected mass) in the case of biodegradation taking place in the vertical flow filter system. Scenario 2 (base case) is highlighted in black.

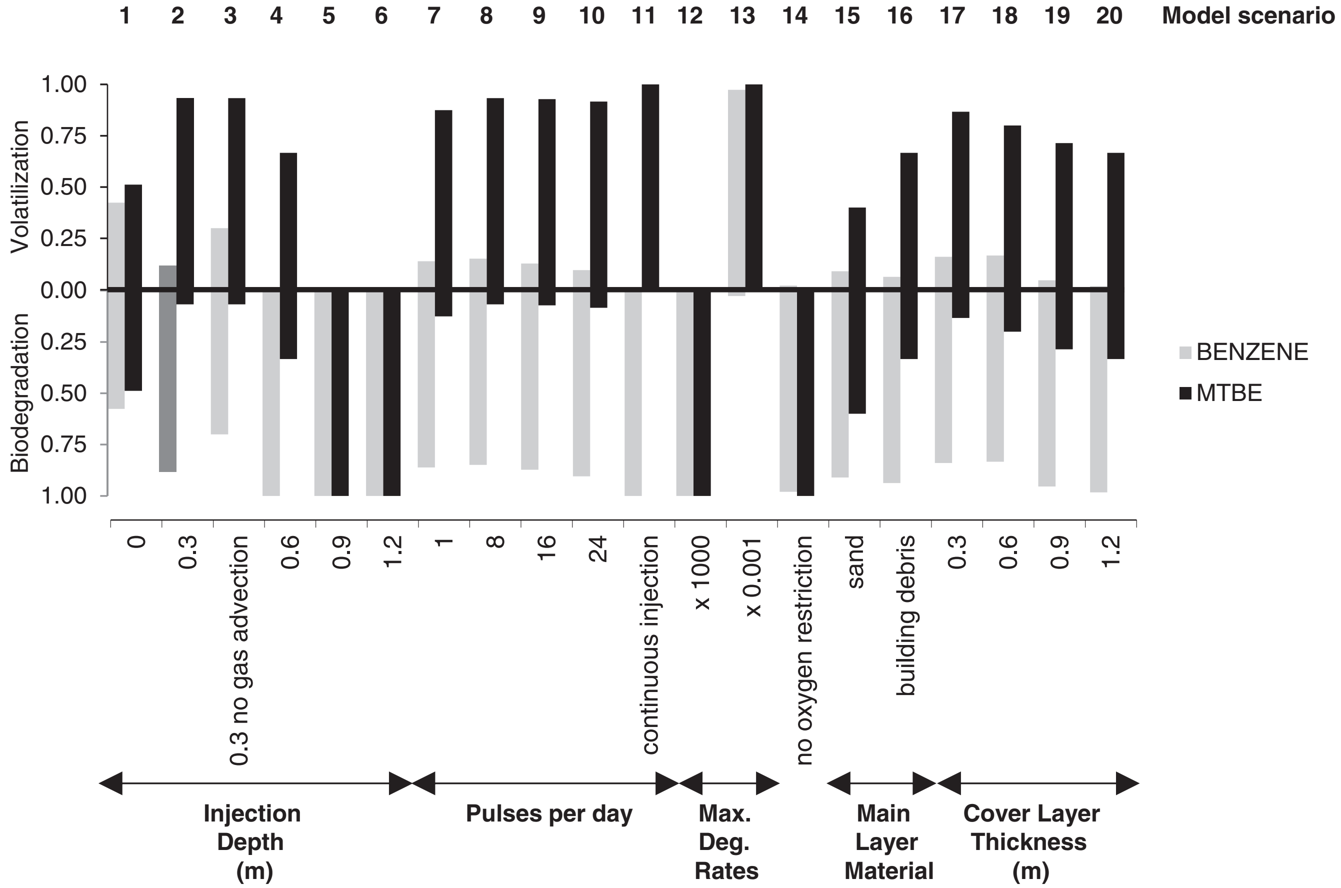

Figure 6. Contribution of biodegradation and volatilization to total removal for the different model scenarios for benzene and MTBE. Scenario 2 (base case) is highlighted in black.

was extended to the top of the injection depth, oxic conditions could (temporarily) penetrate deeper into the filter (Scenarios 2 to 6 and 17 to 20). Exceptions with oxygen penetration significantly deeper than the depth of the water injection could only be found when water was injected on top, when the main layer material was sand (Scenarios 1 and 15), or when decreased biodegradation rates were considered (Scenario 13).

According to Equations 1 to 3, the amount of oxygen needed for complete degradation of the injected groundwater contaminants is 275 mg O_2/L of the treated groundwater. Most of this (202 mg) is required for ammonium, while smaller portions are needed for benzene (62 mg) and MTBE (11 mg). For comparison, the 88 mg/L ammonium in the waste water of the experimental reference required a similar total amount of 296 mg O_2/L.

Discussion

Influence of Gas-Phase Transport on Contaminant Removal

The presented simulation results confirm that the transport of gaseous species in the soil-air phase influences contaminant removal in different ways: high transport rates of oxygen are needed to support biodegradation and high transport rates of volatile contaminants lead to their emission into the atmosphere. Factors leading to enhance transport rates of oxygen, as the type of material used (Wanko et al. 2005), also promote VOC emissions indicated by the high volatilization potential. Those scenarios with higher emissions in the absence of biodegradation (Figures 4 and 6) showed also an oxygen penetration significantly deeper than the injection depth (Figure 7). In turn for scenarios with no or very low volatilization potential oxygen availability was highly reduced too and very little biodegradation took place (Figures 5 and 6). For most of the high volatilization potential scenarios, reduced but significant emission could still be observed in the presence of biodegradation. This further enhanced the coupling between oxygen penetration and availability, as the emitted fraction of the contaminants did not contribute to the consumption of oxygen in the filter system. Consequently, any feature of the filter construction or operation mode promoting gas-phase transport in the filter system leads to an enhanced removal of contaminants. However, such feature might also increase the contribution of undesired VOC emissions to the observed total removal (compare Scenarios 4 to 6 with Scenarios 18 to 20). Simulations show that advective transport processes in the gas phase, caused by the gas pumping effects induced by the water injection pulses, had only little impact on volatiles emissions. Most of the observed gas emissions can be attributed to diffusion. Advective transport facilitates oxygen and contaminant interaction,

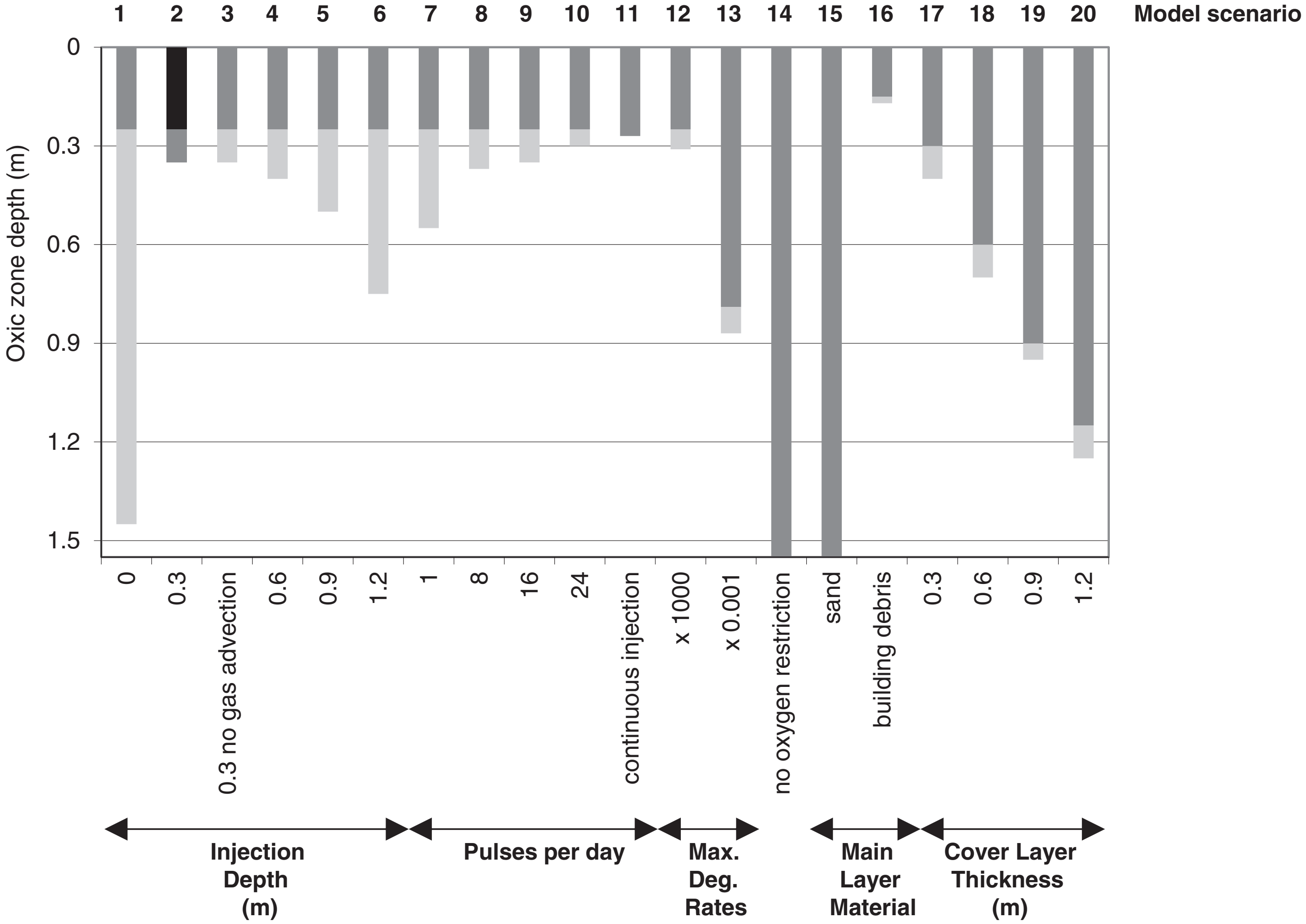

Figure 7. Oxygen penetration depth in the vertical flow filter system. Shaded areas show ranges of temporal variations (maximum and minimum) within each injection cycle. Scenario 2 (base case) is highlighted in black.

and thus triggers removal by biodegradation (Scenarios 2 and 3 in Figures 4, 5, and 6).

Another effect from volatilization and the subsequent transport of species in the gas phase is the extension of the biodegradation zone further up into filter parts above the injection zone. This zone contributed in part to biodegradation in the filter systems as some of the injected water and the contaminants therein migrated upward. For volatile species, the additional gas-phase transport into this zone leads to an enhanced biodegradation of these contaminants. In detail, their re-equilibration with the residual water phase in the upper filter parts and the high oxygen availability allowed for their degradation. This led to oxygen depletion already above the water injection zone, which explains the simulated oxygen penetration depths (partly) not reaching the depth of water injection. Furthermore, biodegradation in these upper parts contributed to the lower VOC emissions observed for each scenario in the presence of biodegradation compared to the maximum potential observed in the absence of biodegradation. The general ability of microorganisms to respond to gas-phase contaminants and to affect their transport at the centimeter scale has been shown in laboratory experiments (Hanzel et al. 2011) and appears to be a controlling factor for the fate of volatilized species in the filter systems.

Influence of Filter Design on Filter Performance

Given the above-described coupling between oxygen availability and volatile emissions raises the question whether a high removal by biodegradation can be achieved in the absence of volatile emissions, and how such conditions can be achieved by optimal combination of filter construction and operation. For most of the simulated scenarios biodegradation was limited by oxygen availability. The latter is also restricted by the water saturation, with an optimal water saturation of around 60% (Kristensen et al. 2010). Oxygen availability is indicated by the limited oxygen penetration depths and by the low sensitivity of ammonium and benzene degradation to an increase of maximum degradation rates (Scenario 12 vs. Scenario 2). Only for MTBE, the least degradable contaminant in this study raising the maximum rate led to degradation increase. In turn, in the absence of oxygen limitations all injected contaminants could be removed (Scenario 14).

Furthermore, for conditions leading to permanently high water saturations, for example, due to a continuous injection (Scenario 11), gas-phase transport was suppressed. This avoided volatilization and due to the lack of oxygen, ceased biodegradation and hardly any removal took place. Also in many other scenarios water saturations were quite high (e.g., Scenario 2; Figure 3), which led to the observed limitations in oxygen availability. Consequently, a filter design which aims at the suppression of volatile emissions by high water saturations would not support sufficient contaminant removal in the filter. For the same reasons, the location of the water injection should not be too far away from the filter top to allow for sufficient ventilation with oxygen. Conditions supporting a sufficient availability of oxygen can be achieved without the occurrence of volatile emissions depending on the degradability of the contaminants and on the overall oxygen demand. The simultaneous influence on the removal of volatile compounds by biodegradation and volatilization was also observed in recent experiments on vertical flow filters, being volatilization the main removal process when contaminated water was in contact with the atmosphere (Eke 2008; Eke and Scholz 2008).

If biodegradation rates are high enough, volatile emissions can be avoided (if the injection does not take place right on top of the filter) as long as oxygen is available (e.g., Scenario 14 and comparison of Scenarios 2, 12, and 13). In such cases, the uppermost part of the filter can be an efficient reactive barrier and high degradation rates do not only lead to a complete removal of the contaminants but also suppress (nearly) any volatile compounds reaching the top of the filter. The importance of high biodegradation rates for the suppression of volatile emissions is also supported by the differences between the two volatile compounds. In the absence of biodegradation, benzene, as the more volatile compound, exhibited a higher potential for volatile emissions than MTBE. But, when considering biodegradation, the higher degradability of benzene allowed for similar or less volatile emissions than observed for MTBE. The relevance of the degradation rate is also highlighted by the similar VOC emissions observed for the base-case Scenarios 2 and 15 considering sand as a main layer material. While the different main layer material affected water saturation, hydraulic residence time and oxygen availability, and thus biodegradation in the main layer, the fate of the volatilized contaminant fraction is hardly changed. The latter is mainly depending on the processes taking place above the water injection zone. Both scenarios present, on this upper part of the filter, enough oxygen and low water saturation, being biodegradation rate the controlling factor for the amount of contaminants reaching the top of the filter.

The overall oxygen demand is determined by the composition of the injected groundwater. In this study, ammonium was considered as additional nonvolatile compound and most of the oxygen demand was attributed to ammonium in order to test the removal performance for volatile compounds at such realistic but nonideal conditions. In the absence of ammonium and any other additional oxygen sinks, less oxygen supply would be needed. This would allow limiting gas-phase transport rates while still achieving sufficient oxygen availability. Accordingly, this would reduce the volatilization potential and emissions could be easily avoided.

The performance of vertical flow filters for the removal of VOCs and thus the applicability of such filter systems for the treatment of groundwater contaminated by such volatile compounds ultimately depend on the amount and degradability of the groundwater contaminants. The amount of contaminants and thus the oxygen demand for their biodegradation can be addressed by filter designs supporting a high oxygen supply. For this purpose, design criteria already in use for the biodegradation of nonvolatile compounds in such filter systems can be applied (i.e., highly unsaturated conditions, good contact to the atmosphere, etc.). However, the treatment of volatiles requires also a sufficiently good degradability of the treated compounds as well as conditions supporting high biodegradation rates in the uppermost part of the filter. In contrast to nonvolatile compounds where low degradation rates could be compensated by increased hydraulic residence times, the suppression of VOC emissions requires operation conditions (temperature, nutrient supply, grain surfaces, etc.) which offer such high biodegradation rates. This is to induce a complete degradation of the volatile compounds while diffusing through the filter passage between the water injection zone and the top of the filter. The optimal length of this filter passage again depends on the total oxygen demand of the groundwater contaminants.

Implications of Model Simplification

To our knowledge, this is the first application of a reactive transport model to assess the fate of volatile compounds in vertical flow filters. Presented results show that simulation approach can support the prediction and evaluation of such filter systems. Nevertheless, the presented model simulations are subject to a number or simplifications. For instance, abiotic reactions such as mineral precipitation and dissolution as well as the formation of microbial biomass were not considered, and consequently hydraulic conductivity changes produced by clogging due to mineral precipitation or biomass accumulation were neglected in the model. Although not reported for the Langenreichenbach reference system, long-term operation of filter systems may lead to such clogging effects (Knowles et al. 2011), but the resulting implications for the filter performance were beyond the scope of this study. The same holds for the simulation of pH and its interaction with the biodegradation of the contaminants.

Calibration of ammonium degradation rate was done without considering other species consuming oxygen in Langenreichenbach. This consideration was made on the assumption that ammonium is the species consuming oxygen fastest in typical domestic waste water and because ammonium was almost completely degraded. The maximum ammonium degradation rate obtained by the calibration is one order of magnitude faster than the degradation rates presented in literature for vertical flow constructed wetland (Langergraber 2001; Langergraber and Šimunek 2005), but the addition of oxygen sink species in the calibration would not have led to lower maximum degradation rates.

MTBE is mainly degradable at aerobic conditions (Fischer et al. 2005), and anaerobic degradation of ammonium and benzene (Wiedemeier et al. 1999) is possible although at much lower rates. Thus, such anaerobic degradation was not included in the model as their potential impact on the removal of the contaminants is rather minor. Additionally, by only considering aerobic degradation the total removal could be easily attributed to the solely effect of oxygen as electron donor in the absence of any other electron donor contributing to the removal.

Air and water diffusion can be specified in the model as only one coefficient for each phase. While diffusion in the water phase is not an important transport process in the presented simulations, the use of a single air phase diffusion coefficient does affect the simulated transport of volatile species. The use of the average for benzene and MTBE as value of the air phase diffusion coefficient allowed for a realistic estimation of volatilization of the volatile compounds but underestimating oxygen diffusion rates and thus biodegradation. Thus, the used values should be considered as conservative estimate concerning contaminant removal by biodegradation and oxygen penetration depths.

The simulations do not consider seasonal temperature variations and precipitation events. While annual precipitation rates are in the order of typically several hundred L/m^2 and thus are small/negligible compared to the injected amounts of water, temperature variations have an effect on Henry's law constants, diffusion coefficients, and degradation rates, and may modify the mass balance of the considered components during the course of the year. Such temperature-induced performance variations may need to be considered for the interpretation of specific filter systems on the base of measured field data. However, for the aim of this study to delineate the general performance of vertical soil filters, a detailed evaluation of temperature changes (in particular seasonal variations) was not the scope. Model simulations are assumed to represent average filter behavior considering average annual temperatures for Central Germany, and the presented conclusions are expected to apply on general aspects of filter performance.

Plant effects were only considered implicitly for the influence of their roots on the hydraulic properties of the filter material while other effects were neglected. This includes root uptake did not exhibit any effect on the water mass balance used for the calibration of the water flow in the Langenreichenbach reference system (Maier et al. 2009). Furthermore, the release of any reactive compounds (e.g., oxygen, root exudates) was found to affect contaminant degradation in vertical filters (Wang et al. 2011). Nevertheless, this is considered to be negligible in this study because of the much higher water turnover in the vertical system simulated here compared with those from related studies.

Summary and Conclusions

The presented model simulations demonstrated that vertical flow filters have a high potential for the removal of volatile groundwater contaminants. The simulated filter systems do also exhibit a significant potential for VOC emissions. Accordingly, because factors enhancing oxygen availability also promote volatile removal through emissions, observed contaminant removal cannot be only attributed to biodegradation. However, if oxygen availability is sufficiently high, VOC emissions can be avoided when biodegradation rates are high enough to counteract the emissions. To achieve this, a combination of different factors is required: the filter design must allow for oxygen transport meeting the total oxygen demand of the groundwater contaminants, and the degradability and the conditions in the filter must support adequately high biodegradation rates in the filter passage between the water injection zone (to be located inside the filter material) and the top of the filter.

The requirements on the filter design to meet the desired oxygen input into the filter are analogous to filter systems used for nonvolatile compounds: filter material and injection scheme promoting low water saturation, as well as good connection between atmospheric conditions on top of the filter and the microbially active zones inside the filter. Together with the total oxygen demand these requirements determine at which depth the water is best injected into the filter. This depth should still allow for a sufficiently high availability of oxygen but also for a maximum length of the travel passage of the volatilized compounds to the top of the filter. During this passage, the volatile compounds are subject to biodegradation, and biodegradation rates control the efficiency of the passage for avoiding VOC emissions.

In case these criteria are met vertical flow filters can be a suitable remediation means for groundwater containing volatile contaminants. Given the scarcity of experimental data on volatile emissions for such filter systems and the challenges associated with such measurements, reactive transport modeling can contribute to test and modify the design of vertical flow filters to achieve a good compromise of conflicting design factors and increase the removal performance while limiting VOC emissions. Once a larger number of sufficient experimental data sets on the contribution of the different VOC removal processes are available, reactive transport modeling approaches can be further tested and validated to allow for more detailed assessments of the fate of VOCs in vertical flow filters.

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