Reactive transport simulation of volatile organic compound removal in vertical flow soil filters

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Abstract Vertical flow soil filters are an emerging technology for the treatment of groundwater contaminated with volatile organic carbon compounds. These filters are characterized by unsaturated flow conditions and high contaminant removal rates, but for the assessment of their remediation efficiency a sound distinction between biodegradation and volatilization is crucial. In this study, a vertical flow soil filter system exposed to intermittent feeding of contaminated groundwater leading to a highly transient flow pattern was simulated using the numerical model MIN3P. Simulated processes include (besides other reactions) the microbial degradation of aqueous species as well as their volatilization and advective-diffusive transport in the water phase and the soil air phase. Flow and transport processes were calibrated using measured field data and the model subsequently used to describe the removal of ammonium and two volatile organic contaminants – benzene and MTBE. Model results confirm experimentally observed high removal rates and show that both removal processes – biodegradation and volatilization – have the potential to significantly contribute to such removal. The contribution of each process depends on the design and operation of the filter system, the hydraulic properties of the filter material, and the degradation capacity of the microbial population. If these factors are sufficiently well combined volatile emissions can be avoided and observed contaminant removal can be nearly all attributed to biodegradation.

Key words reactive transport modelling; volatile organic compounds; unsaturated zone; groundwater remediation; biodegradation

INTRODUCTION

The use of vertical flow filters and vertical flow constructed wetlands for wastewater restoration from different sources has been used since the 1970s (Kadlec & Wallace, 2008). Recently, vertical flow filters have been tested for the removal of organic compounds at the laboratory scale (Eke, 2008; Eke & Scholz, 2008) and also as a groundwater remediation technique at the pilot scale. These pilot scale tests were conducted as part of the SAFIRA-II project (Rügner *et al*., 2007) at a field site in Leuna, Germany, where groundwater is heavily contaminated with hydrocarbons (mainly benzene and MTBE), as well as ammonium. In Leuna, the tested vertical flow filters were fed with regular pulses of contaminated groundwater and showed high organic contaminant removal. An experimental analysis of the contribution of biodegradation and volatilization to the observed contaminant removal is challenged by the high spatio-temporal dynamics of the filter systems: while biodegradation is leading to a desired destructive removal of the contaminants, volatilization can cause an undesired emission of harmful compounds to the atmosphere. For these reasons the experimental analyses are combined with numerical reactive transport simulations to evaluate the relevance of the different processes for overall contaminant removal and to determine factors controlling the contribution of each individual removal process. Reactive transport modelling of vertical flow filters and constructed wetland have been used to reproduce the treatment of domestic wastewater (Langergraber, 2001, 2003, 2008; Langergraber & Šimunek, 2005; Langergraber *et al*., 2007, 2009). Up to now, these modelling efforts were only aimed at reproducing the fate and transport of non-volatile contaminants.

The present study aims at a quantitative analysis of the contribution of biodegradation and volatilization on the overall removal of contaminants in a vertical flow filter system. For this purpose, we use the numerical reactive transport model MIN3P to simulate the fate of two volatile organic contaminants (benzene and MTBE) together with a non-volatile contaminant (ammonium) present in groundwater applied to a vertical flow filter. The simulation of microbial degradation and volatilization of contaminants was combined with modelling the advective and diffusive transport, not only in the water, but also in the gaseous phase of the unsaturated filter system. For a hypothetical system, prediction of such vertical flow filter performance was carried out for different types of operation schemes and filter designs to assess the potential risk of volatile losses to the atmosphere. Subsequently the model concept was applied for the assessment of a pilot scale vertical flow filter from Leuna. The comparison of measurements of reactive species concentrations was accompanied with analyses of conservative tracers and radon as volatile tracer.

MATERIALS AND METHODS

Numerical model used and model set up

The model MIN3P (Mayer *et al*., 2002) was used to perform the numerical simulations. MIN3P allows for the simulation of reactive transport of dissolved and gaseous species under variable saturated flow conditions. The MIN3P version used for the present study considers advective and diffusive transport of gaseous species (Molins & Mayer, 2007, Molins *et al*., 2008, 2010; De Biase *et al*., 2011b).

A preliminary simplified model was set up for simulation under different hypothetical scenarios, where the depth of injection and the number of daily injection pulses as well as the composition of the main filter material were varied to test their influence on the performance of the filter system. For the simplified model, a 1-D vertical structure with a cover, main and drainage layer, using a constant spatial discretization of 1 cm, was used. Parameters used for the different layer material were taken from Maier *et al*. (2009). For temporal discretization a maximal time step of 1 minute was assigned, with the model automatically reducing the time steps if needed to reproduce highly dynamic processes. The depth of injection varied from a few centimeters below the filter surface to 1.2 m (model scenarios 1–5). The number of daily injection varied from 1, 4, 8, 16, 24 to continuous injection (model scenarios 2 and 6–10). The main filter material considered was sand (model scenario 11) and building debris (model scenario 12).

An advanced model set up was used to compare experimental measurements from the pilot scale vertical flow filter from Leuna to modelled results. The advanced model set up consisted in a pseudo-3-D model domain used to simulate half of the pilot scale vertical filter (see Fig. 1) with 0.85 m width, 0.01 m length and 1.55 m depth (sump is not included). Water was injected in an area of 5-cm diameter, between 0.25 m and 0.3 m below the filter surface. Spatial discretization in the vicinity of the injection point was 0.01 m in x- and z- directions, and coarser for the rest of the model, 0.05 m. The third dimension was used to simulate the internal porosity of the clay pellets describing this intra-aggregate domain as an additional model layer. Parameters describing the flow and transport properties of both model domains (inter- and intra-aggregate) were measured or calibrated to reproduce the dynamics of the flow and transport behaviour observed for the filter system. The temporal discretization used was the same as that used in the prediction simulation cases.

Considered reactive processes include the aerobic biodegradation of benzene, MTBE and ammonium, each following Michaelis-Menten kinetics (with respect to the contaminant and to oxygen), the air–water phase exchanges of volatile species assuming an instantaneous equilibration of dissolved and volatile concentration given by Henry’s law, and the radioactive decay of the radon tracer in the aqueous and the gas phase. Degradation rates applied were taken from laboratory experiments (benzene and MTBE (Wendeberg, 2010)) or literature values (ammonium (Langergraber, 2001; Langergraber & Šimunek, 2005)) and then calibrated with field measurements and temperature adjusted.

Vertical flow filter description and operation

The simulated vertical flow filter is a container (1.7 × 2.3 × 1.75 m) filled with layers of granular material, distributed in three layers (Fig. 1): a cover layer (0.25 m thickness, expanded clay, 8–16 mm), a main layer (1.20-m thick, expanded clay, 3–6 mm) and a drainage layer (0.10 m thick, gravel, 8–16 mm). The drainage layer is separated from a sump (0.20 m thick) at the bottom, by a perforated plate. The treated water is injected through two perforated pipes located between the cover layer and the main layer. The pipes distributed the water in hourly pulses at a rate of 20 L min^{-1}. Operation modes (length of the pulses) varied between 10 L h^{-1} and 160 L h^{-1}, and each operation lasted between 3 and 6 months. A detailed description of operation modes and removal performances is given in van Afferden *et al*. (2011). For the present study, experimental results from the operation modes of 20 and 40 L were used as experimental reference for the simulations.

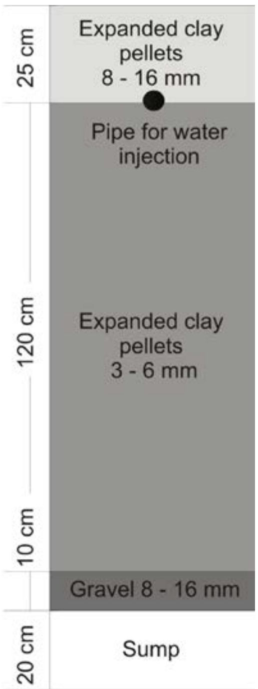

Fig. 1 Schematic cross section of the vertical flow filter.

Dissolved and gaseous tracers tests

Conservative tracer tests were performed in the vertical flow filter to characterize the hydrodynamic properties, mean solute transport velocity and hydraulic residence time for the 20 and 40 L operation mode (De Biase *et al*., 2011b). At each operation mode, a single pulse injection of fluorescein and potassium bromide was performed. The gaseous tracer Radon-222, naturally occurring in the treated groundwater, was measured in the vertical flow filter at the inflow and outflow during for 20 and 40 L operation modes (De Biase *et al*., 2011b).

RESULTS AND DISCUSSION

Model predictions

After the simulated systems achieved a constant daily flow, the transport pattern mass balances were obtained to calculate the percentages the injected amounts of contaminant attributed to the individual removal processes (biodegradation and volatilization; Fig. 2). Simulation results indicated that for the treatment of volatile compounds, the injection of contaminated water a few centimetres below the filter surface prevents a high percentage of volatilization. However, this will also lead to a lower oxygen penetration depth (results not shown) inducing a lower removal of contaminants due to biodegradation (scenarios 1–5). A variation of the daily infiltration pulses will lead to a decrease of the overall removal performance with an increasing number of pulses (scenarios 2 and 6–10), with the lowest performance observed when water is continuously injected (scenario 10). In summary there results suggest that for the considered filter material and injection scheme, biodegradation is severely limited by the lack of oxygen and that increased ventilation of the filter (better gas phase transport) would lead to higher aerobic degradation rates. This is supported by results obtained for using alternative filter materials: while building debris as filter material for the main layer lowers volatilization but does not allow for high biodegradation rates (scenario 12), using sand leads to only a slightly increased volatile removal (scenario 11) but also allows for the highest removal by biodegradation. These results suggest that facilitating gas phase transport between the atmosphere and (all parts) of the filter system is also improving filter efficiency for volatile compounds as the increased availability of oxygen is needed for high biodegradation rates, while the increases in volatile losses are minor. Especially if biodegradation rates are high, major volatile losses can be avoided, even if the potential for high volatilization losses is given (see De Biase *et al*., 2011a for further details).

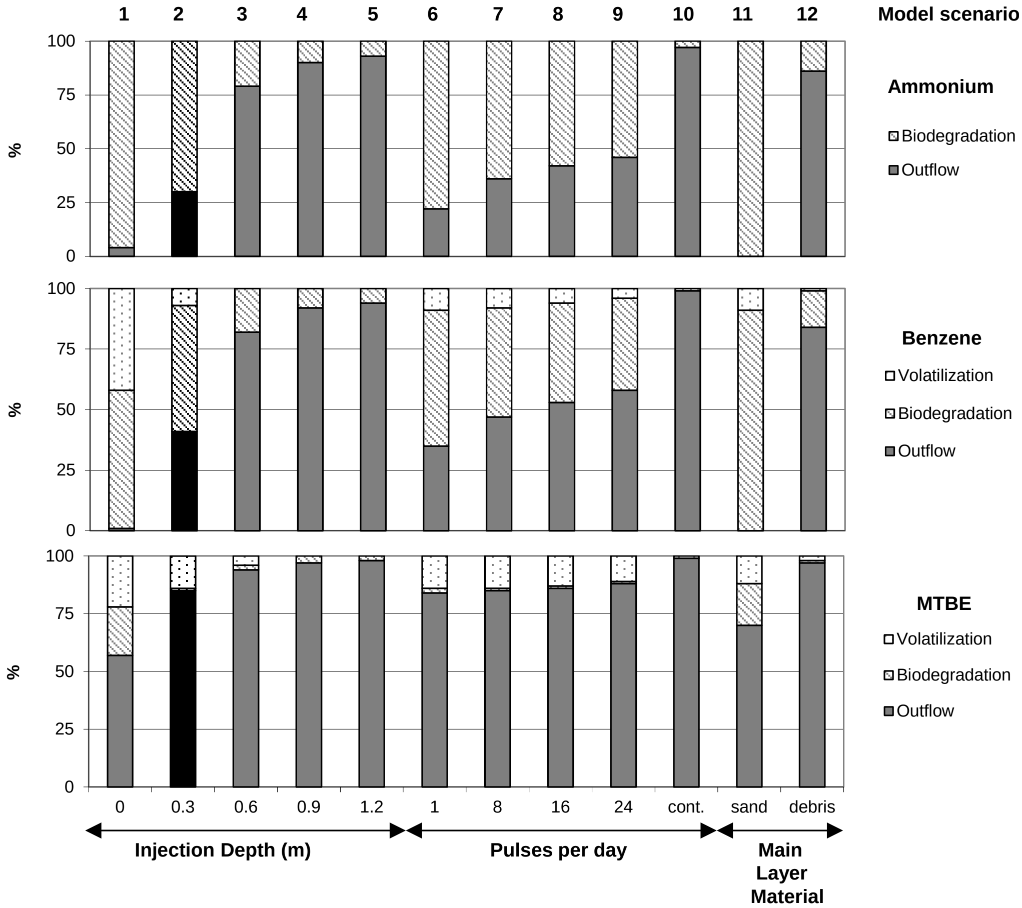

Fig. 2 Mass balance of contaminants (in % of injected mass) in the vertical flow filter for the predicted model scenarios.

Simulation of a pilot scale vertical filter

A comparison between measured and simulated results on water flow and solute transport indicated that the model was able to adequately capture the highly dynamic behaviour of the filter system (Fig. 3). Discrepancies existed mainly for the simulated tracer residence time which is shorter in the model than in the experiments 5 and 3 h compared to 8 and 4 h measured data for the 20 and 40 L, respectively.

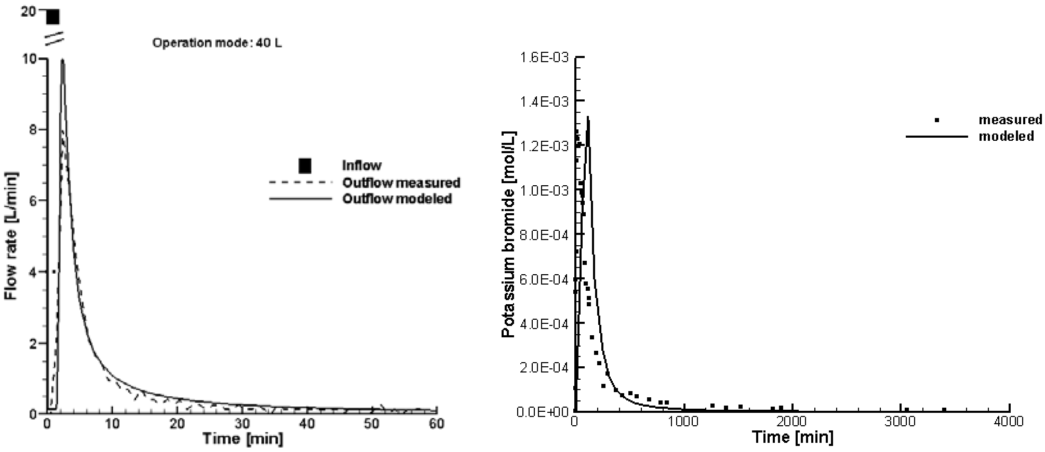

Fig. 3 Measured and modelled outflow rate for operation with 40 L hourly infiltration pulse (left); outflow tracer breakthrough curves (right). Timing and duration of infiltration pulse is indicated via the black bar (■).

For the volatilization and transport of the gaseous tracer Radon-222 the modelled amount of the tracer reaching the outflow was slightly bigger than measured. This is probably due to the shorter residence time of the water in the modelled filter compared to the real filter. This effect might have led to a slight underestimation of the volatilization compared to the real situation.

Using the calibrated flow and transport model, biodegradation rate parameters were adjusted to obtain an agreement between simulated and measured outflow concentrations of the contaminants for the 20 L operation mode. The resulting outflow oxygen concentrations confirm the experimental observation of oxic conditions all along the filter depth. Based on these results the mass balances for the contaminants show that also for the volatile contaminants the high removal rates are mainly attributed to biodegradation with volatilization contributing ≤5% to the overall benzene removal, while MTBE volatilization is nearly negligible (Table 1). Data were then extrapolated to the 40 L operation mode (considering the different average temperatures for both operation periods) and results show that while MTBE removal could be well predicted, degradation rates for benzene and ammonium were higher than modelled values, which were explained by temperature changes alone. Nevertheless, data for the 40 L operation mode also suggest biodegradation to be the dominant removal process, with volatilization contributing even less than for the 20 L mode.

Table 1 Contaminant mass balance in % of injected amounts.

Operation mode	20 L			40 L		
	%Outflow	%Removed		%Outflow	%Removed	
Radon						
Measured	4	96		5	95	
Modelled	7	93		10	90	
Ammonium						
Measured	29	71		26	74	
Modelled	29	71		40	60	
	%Outflow	%Biodeg.	%Volatil.	%Outflow	%Biodeg.	%Volatil.
Benzene						
Measured	2	98		3	97	
Modelled	2	93	5	8	91	1
MTBE						
Measured	9	91		16	84	
Modelled	9	9	0	14	86	0

CONCLUSION

In summary, the numerical model simulation was able to capture the dynamics of the flow and transport of solutes and gases in the vertical flow filter as evidenced by the comparison between measured data and field data. By using reactive transport modelling the quantification of the contribution of each individual process was possible. Numerical model simulation confirmed that volatilization and biodegradation contribute to the removal of volatile contaminants from the groundwater treated in the vertical flow filters, but biodegradation is by far the most important removal process under the circumstances and conditions considered for the present model simulation. Simulations confirm that oxygen supply was enough for the biodegradation of contaminants, implying that high oxygen transfer does not imply high volatilization of organic compounds. Numerical models are powerful tools for the evaluation and effective design of vertical flow filters for the treatment of volatile compounds while preventing undesired contaminant emission to the atmosphere.

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