Design methodology accounting for the effects of porous medium heterogeneity on hydraulic residence time and biodegradation in horizontal subsurface flow constructed wetlands

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ABSTRACT

Horizontal flow constructed wetlands are engineered systems capable of eliminating a wide range of pollutants from the aquatic environment. Nevertheless, poor hydrodynamic behavior is commonly found resulting in preferential pathways and variations in both (i) the hydraulic residence time distribution (HRTD) and, consequently, (ii) the wetland's treatment efficiency. The aim of this work was to outline a methodology for wetland design that accounts for the effect of heterogeneous hydraulic properties of the porous substrate on the HRTD and treatment efficiency. Biodegradation of benzene was used to illustrate the influence of hydraulic conductivity heterogeneity on wetland efficiency. Random, spatially correlated hydraulic conductivity fields following a log-normal distribution were generated and then introduced in a subsurface flow numerical model. The results showed that the variance of the distribution and the correlation length in the longitudinal direction are key indicators of the extent of heterogeneity. A reduction of the mean hydraulic residence time was observed as the extent of heterogeneity increased, while the HRTD became broader with increased skewness. At the same time, substrate heterogeneity induced preferential flow paths within the wetland bed resulting in variations of the benzene treatment efficiency. Further to this it was observed that the distribution of biomass within the porous bed became heterogeneous, rising questions on the representativeness of sampling. It was concluded that traditional methods for wetland design based on assumptions such as a homogeneous porous medium and plug flow are not reliable. The alternative design methodology presented here is based on the incorporation of heterogeneity directly during the design phase. The same methodology can also be used to optimize existing systems, where the HRTD has been characterized with tracer experiments.

KEYWORDS

Hydraulic residence time distribution, sand filter, treatment efficiency, benzene, reactive transport modeling, wastewater treatment, optimization.

1. Introduction

The use of subsurface flow constructed wetlands and sand filters as wastewater treatment technology has been steadily increasing over the last two decades (Vymazal and Kröpfelová, 2008). These systems are appealing because they require only a moderate energy input and are low-maintenance. Wastewater flows through a porous substrate where biological and inorganic reactions transform and remove the contaminants (Kadlec and Wallace, 2009). Depending on the flow direction, subsurface flow constructed wetlands (CWs) are further classified as horizontal (HSCWs) or vertical flow. In HSCWs the porous substrate is water-saturated except for the uppermost layer. Instead, in vertical flow constructed wetlands the bed is variably saturated.

HSCWs have been successfully employed to remove classical contaminants from wastewaters, such as the organic load, nutrients (mainly nitrogen and phosphorous) and pathogens (Caselles-Osorio and García, 2006; Akratos and Tsihrintzis, 2007; Vymazal, 2007; Reinoso et al., 2008; Stott et al., 2008; Kadlec, 2009). Recently, several studies have reported the use of constructed wetlands for removing emerging pollutants, such as pharmaceuticals and personal care products, hydrocarbons as well as other organic compounds (Wallace, 2001; Matamoros and Bayona, 2006; Matamoros et al., 2007a, 2008; Lin et al., 2008). Overall, these works observed that this technology is potentially suitable to degrade even recalcitrant contaminants if present at low concentrations. However, the conditions for the transformation reactions are often sub-optimal and high degradation rates are seldom achieved, even for traditional contaminants (Hench et al., 2003; Kadlec, 2003). The low removal efficiency has been attributed to several reasons, including incomplete understanding of the purification mechanisms (Haberl et al., 2003; Imfeld et al., 2009) and the non-homogeneous distribution of the porous substrate. This latter leads to poor hydrodynamic behavior of the system, which results from a broad distribution of the hydraulic residence time (HRT) and associated preferential flow paths (Suliman et al., 2005; Knowles et al., 2008; Mena et al., 2008; Ascuntar-Rios et al., 2009). This aspect appears to be critical in particular for HSCWs where the treatment efficiency decreases significantly compared with vertical systems (Matamoros et al., 2007b, 2008).

In order to understand the hydrodynamics of constructed wetlands, characterization of the subsurface flow paths using tracer experiments is useful (King et al., 1997; Grismer et al., 2001; Muñoz et al., 2006). For an ideal, homogeneous porous medium, symmetric Gaussian breakthrough curves (BTCs) are produced (Kadlec and Wallace, 2009). However, in practice, multiple peaks, spreading and asymmetric BTCs are frequently observed indicating a complex hydrodynamic flow field (Barry, 1990; Bajracharya and Barry, 1997; Kamra et al., 2001). Preferential flow paths in the subsurface, for instance, can lead to considerable variability in the HRT. The heterogeneity of the filtering media is due to multiple factors, including (i) changes in porosity and (ii) grain size distribution, (iii) presence of plant roots and rhizomes, (iv) biological, physical and chemical clogging and (v) variations induced by different packing and compaction of the bed (Persson et al., 1999; Rash and Liehr, 1999;

García et al., 2004; Małoszewski et al., 2006; Kjellin et al., 2007; Brovelli et al., 2009; Leverenz et al., 2009).

Tracer experiments to study the factors controlling the porous medium heterogeneity in HFCWs were conducted by Suliman et al. (2005). They reported that hydrodynamics in HSCWs becomes more complex as the scale of the system increases, behavior that is also found in natural aquifers (Gelhar et al., 1992). Suliman et al. (2006a,b) also investigated the effect of the inlet position on the hydraulic performance of HSCWs, while the effect of the different filling configurations of the wetland was reported by Suliman et al. (2007). A correlation between the hydraulic residence time distribution (HRTD) and the extent of heterogeneity was observed and it was found that filling the system in vertical sections led to better hydraulic efficiency. Małoszewski et al. (2006) investigated the variability of hydraulic parameters in gravel cells. The hydraulic conductivity was found to vary in the vertical direction, resulting in heterogeneous transport parameters and leading to an uneven flow pattern and HRT variability. A common finding of these works is that porous medium heterogeneity controls the HRTD and, consequently, the treatment efficiency of subsurface flow constructed wetlands and sand filters. More specifically, the treatment efficiency of HSCWs is correlated to the HRT (Chin, 2006; Kadlec and Wallace, 2009). The relationship can be understood considering that pollutant elimination occurs only if the contact time between active microbial biomass and contaminated water is sufficiently long to promote the biological and abiotic reactions able to remove the contaminant from the water.

If treatment efficiency is a function of the HRT alone, it follows that the optimal efficiency is achieved when the HRTD is narrow, a situation that is approached most closely in a homogeneous medium. However, this rarely occurs thereby resulting in suboptimal treatment efficiency (Persson et al., 1999; Chazarenk et al., 2003; Jenkins and Greenway, 2005). Correct sizing of HSCWs during the design phase is therefore of paramount importance to guarantee high removal rates and good functioning in a wide range of operational conditions. To date, however, dimensioning is still mostly based on empirical rules, such as the surface-area-per-equivalent-person criterion. A notable exception is the *P-k-C** model of Kadlec and Wallace (2009). Their approach is derived from the tank-in-series model, and it is particularly appealing because combines simplicity with the ability to incorporate the stochastic variability of the treatment efficiency due, among other reasons, to variations in retention time. HSCWs are becoming increasingly used in more critical applications and to remove emerging contaminants (i.e., organic compounds). As a consequence, traditional design methods may not be suitable to guarantee high water quality levels and new and more robust design tools are sought (Kadlec, 1997). While the connection between the heterogeneous distribution of the hydraulic conductivity, HRTD and removal efficiency is now widely recognized (Marsili-Libelli and Checchi, 2005; Suliman et al., 2005; Wörman and Kronnäs, 2005), it is not known how the design process can be improved to take it into account, and how the negative or positive effects of heterogeneity in working systems can be controlled. Numerical models have been extensively used in numerous applications in the field of the environmental sciences and engineering (such as hydrogeology, soil science, petroleum engineering, etc.) to analyze the effect of heterogeneity on solute transport and biogeochemical reactions. The chemical, physical and biological processes responsible for wastewater purification in CWs are the same as those that produce, for example, organic matter and nutrient transformations in soils and aquifers. Therefore, the same concepts and the same numerical tools developed in these fields can be applied to study CWs. Despite this similarity and the availability of numerous commercial and open-source numerical tools (http://water.usgs.gov/software/lists/groundwater/, http://www.pmwin.net/, http://www.goldsim.com/Content.asp?PageID=26, http://www.pht3d.org/, amongst many others), modeling of wastewater purification in CWs is still limited to the extent that detailed model-based design is far from commonplace. Some emerging models are now available in the literature and have shown that they can be successfully applied to full-scale CWs (e.g., Dittmer et al., 2005; Mayo and Bigambo 2005; McGechan et al., 2005; Langergraber, 2007, 2008; Langergraber et al., 2009a; Toscano et al., 2009; Giraldi et al., 2010). The concept and processes linked to heterogeneity are however not addressed in these approaches. The aim of this work is therefore to analyze the relationship between amount of heterogeneity, HRTD and removal efficiency, and to develop a suitable methodology to incorporate heterogeneity into the design phase. In particular, er to show that process-based design of CWs can be effectively conducted using readily available numerical tools, the strategy presented in the following makes use of a combination of techniques and numerical models developed in other fields that can be readily applied to this type of wastewater treatment system.

2. Methodology

The methodology proposed in this work to study the effect of heterogeneity and to improve the design of constructed wetlands and sand filters combines two concepts. The first is that of the target HRT (or THRT), which is the shortest HRT such that a system will degrade a given contaminant below a target concentration. In real systems treating wastewaters with a large spectrum of pollutants, the THRT is controlled by the most recalcitrant and toxic contaminant, for which the allowed effluent concentrations are lower. The THRT is linked to the contaminant degradation rate, which in turn depends on biomass capabilities and on the environmental conditions of the porous bed (e.g., oxygen availability, temperature, etc.). The THRT can be estimated from previous experience, and further can be corroborated and integrated using numerical models able to reproduce the complex biological transformations occurring in the wetland (Langergraber et al., 2009a). The second concept concerns the HRTD. The HRTD depends on the physical properties of the wetland, and on the hydraulic conductivity distribution and the influent rate in particular. Indeed, the methodology described below is based on the assumption that the treatment efficiency is a function of the HRTD.

While the inflow rate is a design parameter and can be controlled at least to some extent, the hydraulic conductivity distribution is difficult to know a priori with sufficient detail to be used in a standard design approach. To overcome this difficulty, the variability in the hydraulic conductivity distribution is characterized using a numerical stochastic approach. The underlying assumption is that the hydraulic conductivity distribution is spatially correlated and the resulting field can be represented as a random function, characterized by a limited number of parameters. This has been recently confirmed in numerous experiments where it was also shown that the spatial correlation depends on the filling configuration (Suliman et al., 2007). The methodology proposed to incorporate the effect of heterogeneity is given by the following steps:

1. A THRT is defined depending on the most persistent contaminant, or the contaminant for which the smallest concentration in the discharged water is needed. That is, it is the smallest HRT for which water quality standards of the effluent from the system would be satisfied. This parameter can be defined based on past experience (literature data), small scale experiments and/or mechanistic numerical modeling of the degradation processes.
2. Numerical simulations are conducted to evaluate the HRTD of a given system (defined by classical design parameters, such as the loading rate) considering multiple realizations of the same hydraulic conductivity distribution (i.e., every realization of the hydraulic conductivity field has the same statistical properties). At this stage, the system considered has the largest dimensions that can be allowed in reality, and the goal of the methodology is to identify if and to what extent they can be reduced to achieve the target effluent concentration. The hydraulic conductivity distribution depends on the physical properties of the porous medium (e.g., spatial variations in the grain size distribution) and on the strategy used to fill the HFCW basin (Suliman et al., 2007). This latter aspect can however be controlled during construction. How a random hydraulic conductivity distribution can be generated, and how its parameters are defined will be discussed in the following.
3. Combining the outcome of the simulations with the THRT, the probability of failure of the system (PFS) at a given distance from the inlet can be computed. For example, if 10 realizations of the hydraulic conductivity field are used, and at one location in eight cases the observed mean HRT is larger than the THRT, then the PFS is 0.2. The PFS is a metric that indicates how likely it is that the target contaminant concentration will be

obtained at a certain distance from the inlet. It can be computed for a given system using the method presented in point 2 above (and discussed in more detail in §2.4).. The methodology presented here only accounts for the variations in hydraulic residence time. In reality, however, there is a second important source of uncertainty, that is, stochastic variability of the degradation rates (e.g., Kadlec and Wallace, 2009). While this aspect was not considered, the method presented in this work can be further extended to include it, although at the cost of additional complexity.

4. The sizing of the system is based on this information. Ideally, the size will achieve a PFS of 0, meaning a probability of 100% to achieve a given elimination goal. In other situations, for example when the loading rate considered is at one extreme end of the expected range, a larger PFS could be used, in order not to over-dimension the system. Furthermore, there could be situations where the maximum possible dimensions do not suffice to guarantee that the target concentration is achieved. In these cases, alternative options must be considered (e.g., the loading rate must be reduced to increase the HRT, a different treatment technology should be employed, discussion with the local authorities to accept the predicted efficiency of the system, etc.). This is a classical procedure in probabilistic environmental risk assessment approaches (Barnett and O'Hagan, 1997; Rossi et al., 2009).

The same approach can also be used to optimize the performance of working systems. First, the HRTD is characterized using tracer experiments, and the inflow rate is reduced consequently to achieve the THRT. The underlying assumption of this procedure is that the HRT and the flow rate are linearly correlated. This is clearly true in homogeneous conditions since the flow rate can be described using Darcy's law. In more complex situations, where the flow field is irregular due to heterogeneity, diffusion of solutes into the low conductivity (or stagnant) zones might become important and modify the linear scaling of the contaminant residence time with the inlet flow rate (or the hydraulic gradient). The validity of this assumption will be tested in the following.

2.1 Test case set-up

A realistic test-case was developed to illustrate the methodology and analysis of the relationship between porous medium heterogeneity, HRTD and treatment efficiency. While the analysis presented in the following is relevant to a specific case, the approach can be applied to any contaminant undergoing kinetic degradation in the treatment system. Moreover, in terms of the understanding of the relationship between the heterogeneous hydraulic conductivity, HRTD and treatment efficiency, the findings are also not restricted to the specific set-up used here.

A 10-m long and 1-m deep HSCW was considered in all the simulations presented in this work. Since the goal of our approach is identify the optimal size for the system (in this case only the dimension along the flow direction will be adjusted), the chosen length represents the upper length limit. In other words, the optimal length will be selected based on the analysis that follows, but cannot be longer than 10 m. This upper limit can be in practice decided depending on the available space or considering economic constraints. For the sake of simplicity and to keep the computational effort moderate, we only consider a two-dimensional vertical cross section of the system to be modeled. Preliminary numerical experiments were conducted to evaluate whether heterogeneity in the transverse horizontal direction affected the HRTD. It was observed that, while it has an effect, it is nearly the same as the influence of the heterogeneity in the vertical direction and for this reason a two-dimensional cross-section suffices. Nonetheless, a two-dimensional flow system is known to give different results to a three-dimensional system. For example, Dagan (1989) has shown for an isotropically (referring to correlation length) log-normally distributed hydraulic conductivity that the effective hydraulic conductivity is always the corresponding geometric mean in two-dimensions and is always greater than the geometric mean in three dimensions, at least for spatially infinite domains. Thus, for such a medium, it is expected that the HRT is always greater in two dimensions than in three dimensions, other things being equal. Put another way, the three-dimensional system usually has more degrees of freedom in terms of flow paths through it, in which case the effective hydraulic conductivity would normally be expected to be greater than in two-dimensions. For finite domains, such as that considered below, it has been found that the effective conductivity is expected to be higher than the geometric mean (Hristopulos, 2003). This result was found in the numerical results reported below.

A summary of the dimension and key parameters of the model is given in Table 1. Head boundary conditions were used at the inlet and outlet, while a no-flow condition was set at the bottom. Numerical simulations were conducted using a modified version of the saturated flow and reactive transport code PHWAT (Mao et al., 2006; Brovelli et al., 2009). This model incorporates MODFLOW-88 (McDonald and Harbaugh, 1988) to simulate water flow in saturated porous media and MT3DMS (Zheng and Wang, 1999) for multispecies solute transport. Biological degradation reactions were computed using a purpose-built module that solves numerically the system of coupled ordinary differential equations using an explicit Runge Kutta scheme with adaptive time stepping (Brovelli et al., 2009).

Numerical experiments were initially conducted to verify that simulation results were independent of the selected discretization and model setup. This included grid convergence analysis to verify that the selected spatial resolution did not introduce numerical artifacts, and evaluation of the operator splitting error to identify the optimal time stepping. To avoid dependence on specific initial conditions all the simulations were run starting with a small initial biomass concentration and full oxygen saturation, and results were studied only when the spatial distribution of benzene (see next section), oxygen and biomass reached steady-state. It was observed that in all the model runs, including those with large heterogeneity, steady state was achieved after 30 d of simulated time. Furthermore, since a Monte Carlo approach is used to evaluate the effect of heterogeneity on the HRTD and treatment efficiency, numerical experiments were conducted to define the number of realizations needed to obtain statistically significant results. It was found that for each case with heterogeneity at 30 realizations were sufficient to get a stable mean and standard deviation of the model output, and this value was used throughout the work.

2.2 Biological transformations

The test case considers design of a system to treat wastewater contaminated by benzene. Benzene is a priority substance in the European Water Framework Directive because it is widespread and poses serious risks for the environment, being highly toxic, carcinogenic and, depending on the conditions, recalcitrant (e.g., Prommer et al., 2000; Johnson et al., 2003). Engineered constructed wetlands are a suitable technology for removing benzene from contaminated waters (e.g., Moore et al., 2000; Wallace, 2001; Dittmer et al., 2005; Wallace and Kadlec, 2005; Bedessem et al., 2007; Eke and Scholz, 2008; Tang et al., 2008, 2009; Reiche et al., 2010; and the summary presented in Kadlec and Wallace, 2009, pp. 518-519). A critical aspect that must be considered for HSCWs is the development of anoxic conditions when the organic load is high. This can be avoided for example through the addition of an aeration device (e.g., Wallace and Kadlec, 2005). Moreover, benzene is well suited for the illustrative purposes of this example, in that its degradation rate is strongly reduced as the oxygen concentration is reduced, and therefore the degradation efficiency becomes very sensitive to the effect of heterogeneity.

In this work the approach of Robinson et al. (2009) was followed to model aerobic degradation of benzene:

$$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O. \tag{1}$$

Oxygen was the only electron-acceptor considered, and the attenuation rate of benzene, R_B was defined using a Monod-type equation (e.g., Prommer et al., 1999; Barry et al., 2002):

$$R_B = \frac{\partial C_B}{\partial t} = -\mu_{max,B}\left(\frac{C_B}{K_{S,B}+C_B}\right)\left(\frac{C_O}{K_{S,O}+C_O}\right) I_{bio} X_b, \tag{2}$$

where X_b is the biomass concentration, C_B, $\mu_{max,B}$ and $K_{S,i}$ are the concentration, maximum degradation rate and half-saturation constant of component i and the subscripts B and O stand for benzene and oxygen, respectively. As the biomass fills the pore-space the benzene degradation rate is progressively reduced because the availability of oxygen and nutrients in the biofilm becomes diffusion-limited (Prommer and Barry, 2005). The model takes in to account this reduction with the inhibition term I_{bio} (Brovelli et al., 2009):

$$I_{bio} = \frac{X_b^{max} - X_b}{X_b^{max}}, \tag{3}$$

where X_b^{max} is the maximum amount of biomass that the pore-space can host. This parameter was computed assuming a residual porosity of 0.05 (i.e., at least 5% of the pore-space always remains free), with the biomass mass composition and dry density taken from the literature, see Table 2 (Orhon and Artan, 1994, Brovelli et al., 2009).

While benzene is degraded oxygen is consumed and fresh biomass is produced:

$$\frac{\partial c_O}{\partial t} = S_B R_B, \tag{4}$$

$$\frac{\partial X_b}{\partial t} = Y_b R_B - k_d X_b, \tag{5}$$

where S_B is the stoichiometric coefficient of benzene degradation, Y_b is the biomass yield coefficient related to the consumption on benzene and k_d is the first-order biomass decay coefficient. Model parameters were taken from the literature and are typical values for field-scale applications (e.g., Wynn and Liehr, 2001; Rousseau et al., 2004, Gödeke et al., 2008). A summary of the kinetic parameters and stoichiometric factors is reported in Table 2.

2.3 Influent and target effluent concentration

The influent concentrations of benzene and oxygen are reported in Table 2. The inflow is oxygen-saturated, a typical condition for wetlands treating benzene (Wallace and Kadlec, 2005), while the benzene concentration was chosen so that oxygen is never completely depleted. Because of this, oxygen remains as the sole electron acceptor in the system.

Two target concentrations were considered. The first target is 90% removal efficiency, which corresponds to 3.5×10^{-6} mol l^{-1}. That is, the metric is met when the benzene concentration in the discharged water is equal or smaller than 10% of the influent concentration (OEaux, 2008). Following the World Health Organization guidelines (World Health Organization, 2006), a second and more restrictive target value was selected, equal to a concentration of benzene of 0.01 mg l^{-1} (1.3×10^{-7} mol l^{-1}). This value is conservative and is the concentration limit for drinking water. While such a low value might be difficult to achieve, it will be used to illustrate how the approach presented also allows the definition of situations where the use of this wastewater treatment technology is not suitable due to a high probability of failure.

2.4 Random hydraulic conductivity fields

The key feature of the design methodology is that the effect of heterogeneity is directly addressed making the hydraulic conductivity variable in space. Based on numerous case studies at the field and laboratory scales it is often assumed that hydraulic conductivity follows a log-normal distribution (e.g., Kottegoda and Katuuk, 1983; Hamed et al., 1996; Skaggs and Barry, 1997). The two-dimensional hydraulic conductivity random field is often parameterized using four variables, namely the mean and variance of the hydraulic conductivity distribution, and the correlation lengths in the longitudinal and transverse directions. The mean and the variance control the interval in which the hydraulic conductivity can vary. The correlation lengths and the ratio between the transverse and longitudinal length scales (the aspect ratio of the field) instead define the spatial structure, a critical factor for the HRTD. The effect of the correlation distances is exemplified in Fig. 1, where two realizations with different aspect ratios but same mean and variance are plotted. In both realizations the same transverse correlation length is used, and in both the longitudinal (horizontal, in the direction of the flow) correlation is larger than in the transverse direction. In the top panel, however, the aspect ratio is about 0.15, whereas in the bottom panel it is an order of magnitude smaller (0.018). The comparison shows that, as the longitudinal correlation increases (and so the aspect ratio decreases), the hydraulic conductivity field becomes more stratified with horizontal flow paths tending to connect directly the inlet to the outlet. This decreases the mixing of water in the porous bed and allows faster discharge of the polluted water. When the longitudinal correlation is short compared to the scale of the wetland, the extent of the preferential flow paths is instead limited and good mixing (and therefore high removal of the pollutants) is still possible.

The hydraulic conductivity fields were generated using a tool based on Mejia's algorithm (Mejia and Rodriguez-Iturbe, 1974) developed by Frenzel (1995) and included in the PMWIN software (Processing Modflow for Windows) (Chiang, 2005). Twelve cases were studied having different standard deviations and correlation lengths. However, only four cases are informative so only those are reported and discussed in the following. A summary of the features of the four random hydraulic conductivity fields is given Table 3. All the cases had the same mean value (20 m d^{-1}, consistent with the homogeneous case and corresponds to a clean sand or sand/gravel porous medium, Bear and Verruijt, 1986), while the standard deviation of the log-normal hydraulic conductivity distribution was varied. More specifically, in two of the cases reported in the following the standard deviation was set to 10% of the mean hydraulic conductivity, while in the remainder it was set to 20% of the mean. These values were selected to keep the resulting hydraulic conductivity in a reasonable interval, as would be expected for a (relatively homogeneous) constructed wetland. For example, when the standard deviation is 20% of the mean, the resulting hydraulic conductivity varies in the range 0.1 to 120 m d^{-1}. A larger interval is likely not realistic because the porous media used as substrate for the treatment system are relatively coarse and the grain size distribution is narrow. The only mechanism that might further alter the hydraulic conductivity is biological activity (microbial growth, plant roots and rhizomes) that can clog the pore space or create cracks and preferential flow paths. These processes were however neglected in this work and therefore larger hydraulic conductivity ranges were not considered.

The four cases considered all have the same correlation length in the transverse (vertical) direction because it was found that this parameter had only a small influence on the HRTD. The longitudinal correlation is instead more important, and the two values used were selected to show the effect of a longitudinal correlation (i) shorter and (ii) comparable to the size of the wetland in the flow direction.

Finally, it should be noted that while the method used in this work to create the random hydraulic conductivity fields is one of the most popular, other approaches – sometimes more sophisticated – are available. The design methodology presented is independent of the approach used to generate heterogeneous distributions of the hydraulic properties.

3. Results and discussion

3.1 Conservative tracer and HRTD

Tracer experiments with continuous injection of a conservative non-retarded tracer were simulated to study how heterogeneity affects the HRTD. Tracer BTCs are shown in Fig. 2, where the normalized tracer concentration is reported as a function of the number of pore volumes (PV). One PV corresponds to the nominal HRT, computed assuming homogeneous conditions. The homogeneous case (named as Case H in this and following figures) is compared with the two cases with short (left panel) and long (right panel) correlation lengths. The homogenous case has a symmetric shape and almost no tailing, whereas the BTCs for the heterogeneous cases indicate a more complex hydrodynamic behavior, suggested by the longer tailing and the faster initial discharge. It is well known (e.g., Kreft and Zuber, 1978; Parker and van Genuchten, 1984; van Genuchten and Parker, 1984; Parlange et al., 1985, 1992; Barry and Sposito, 1988) that the applied boundary conditions can have a small effect on BTCs but it is clear from Fig. 2 that the medium heterogeneity has a much more significant effect.

A convenient means to analyze the results in Fig. 2 is to convert the tracer BTCs in to the corresponding HRTD (Fig. 3), computed as the time derivative of the normalized BTC. The HRTD's for heterogeneous conditions differ drastically to that for the homogeneous case. In the homogeneous case the peak is symmetric and sharp, with a maximum that corresponds to the nominal residence time (one PV). As the amount of heterogeneity increases (Cases 2 and 4) the position of the maximum is shifted towards shorter times, and both the spreading and the skewness of the HRTD increase. The effect of heterogeneity on the residence time can also be deduced from the computed effective (bulk) hydraulic conductivity of the four cases. These values are given in Table 3, where the mean and standard deviation for the 30 realizations are reported. For each realization the effective conductivity was computed from the total water flow across the simulated wetland using Darcy's law. The effective conductivity is larger than the mean value in all cases with heterogeneity, as expected and as predicted from the BTCs. These results further stress the importance of the longitudinal correlation length on the residence time because, with the same variance (cases 2 and 4), the effective hydraulic conductivity for the case where the longitudinal correlation length is similar to the scale of the system is nearly twice that for the case with the short correlation length.

The results of the simulations show that the values of both the variance and correlation length produce different hydraulic conductivity patterns and hence BTCs. As the variance of the log-normal distribution increases the hydraulic conductivity field can have larger values, while a high longitudinal to vertical correlation length ratio (i.e., small aspect ratio) tends to create preferential flow paths (see the random field shown in the lower panel of Fig. 1 where high conductivity channels can be observed). The BTCs in Figs. 2 and 3 resemble those that are produced by the two-region (or mobile-immobile region) model (e.g., Coats and Smith, 1964; Li et al., 1994; Griffioen et al., 1998). Indeed, Bajracharya and Barry (1997) used a similar Monte Carlo approach to that presented here in order to relate empirically the two-region model parameters to those of the hydraulic conductivity field.

Fig. 4 shows instead how the HRTD varies as the tracer moves from the inlet to the outlet in the simulations with larger amount of heterogeneity. This figure shows the mean HRT (50% of the mass of solute passed a given location) and the upper and lower 0.05 percentiles, which indicate the time required for 5% and 95% of the mass of solute to pass through a certain cross-section. In other words, for a certain cross-section, at the time indicated by the upper 0.05 percentile, 95% of the mass of solute is still in between the inlet and the cross-section, and vice-versa. In homogeneous conditions the HRT increases linearly with the distance from the inlet (recall water flow is described using Darcy's law) and is controlled by the hydraulic conductivity. Fig. 4 confirms that even with heterogeneity the HRT overall increases linearly as the water moves from the inlet to the outlet, although the slope of the lower 0.05 percentile shows some limited variability. Consistent with the BTCs in Fig. 3, the spreading of the HRTD is not symmetric around the mean value, as it would tend to be for a homogeneous hydraulic conductivity. Moreover, the deviation from the ideal, symmetric case (in other words, the skewness of the BTC) increases with the distance from the inlet. This indicates that the effect of heterogeneity is scale-dependent, as already known theoretically (e.g., Dagan, 1984), in aquifers (e.g., Barry et al., 1988; Barry and Sposito, 1990) and from the experimental findings of Suliman et al. (2005).

3.2 Biological transformations

Following the analysis of the changes in the HRTD resulting from heterogeneous distribution of the hydraulic properties, their effect on the microbial transformations was studied. Fig. 5 reports the depth-averaged steady-state distribution of benzene, oxygen and biomass in the constructed wetland. The simulated values were normalized using the initial concentration for benzene, the maximum solubility for oxygen and the maximum amount of biomass that the porous medium can host before becoming clogged (see §2.2). The focus of this work is not to study benzene degradation in constructed wetlands, but to evaluate the differences in terms of biological processes and contaminant degradation rate with and without heterogeneity, and so simplifying modeling assumptions have been employed. In particular, it is assumed that the only oxidizable component in the system is benzene, while in reality other such components are likely to be present in the influent water. Fig. 5 compares the results for the two cases with larger variance (Cases 2 and 4, respectively) with the results obtained considering a homogeneous hydraulic conductivity. For the two cases with heterogeneity the average value of the 30 realizations is reported (dashed line), as well as the standard deviation (area shaded in gray). In the homogeneous case, three regions are observed where the three components show similar behavior. In the first region (fractional distance in the range 0 to about 0.2), the biomass density is constant and is equal to the maximum value (defined by the available pore-space, see Eqs. 2 and 3). Since biomass cannot grow any further benzene and oxygen are exclusively consumed to replace the biomass undergoing cellular lysis. Therefore, the consumption rates are constant (recall biomass decay is modeled as a first-order kinetic process), and the concentration of both oxygen and benzene decrease linearly. In the second region (in the range 0.2 to 0.25 of relative distance from the inlet) the three components show a sharp decay. In this part of the system biomass growth is not limited by the pore space availability (i.e., $I_{bio} \approx 1$), the concentrations are such that the biomass growth and decay rates are in equilibrium, and therefore both oxygen and benzene are quickly depleted and the concentration of the substrate drops by about one order of magnitude within about 0.1 m. This is due to the rather high maximum degradation rate. In the third region, from 0.25 to the outlet, the concentrations of the three components show a very smooth variation, because the availability of both benzene and oxygen becomes the factor limiting the biodegradation rate. The oxygen concentration is reduced to about 10% of the initial value (the solubility limit) but is not completely depleted, i.e., the system never becomes strictly anaerobic.

Simulations with heterogeneity show very different behavior. In both models (Case 2 and 4), the change in concentration of the three components with the distance from the inlet is smoother, and biomass growth near the inlet is reduced compared to the homogeneous case. The standard deviation generally increases with the distance from the inlet, and becomes very large for benzene (and oxygen) in Case 4. This means that the same change in flow or HRT (the heterogeneity is statistically homogeneous within the wetland and among the different realizations) has a stronger impact when the degradation rate is reduced, and indicates that systems designed to treat recalcitrant compounds are more sensitive to heterogeneity than systems where the substrate is easily biodegraded.

The steady-state depth-averaged profiles cannot be easily explained considering the biological processes only, as was done for the homogeneous case. In the heterogeneous case the spatial distribution of solutes and biomass is controlled by the flow patterns. This can be observed in Fig. 6, where an example of the real biomass distribution in the simulations with heterogeneity is shown. Once again, in this plot the biomass is normalized using the maximum biomass density that the porous medium can host. Fig. 6 shows that biomass developed in a complex and unpredictable pattern, with variations as large as two orders of magnitude in the transverse direction. The biomass distribution map reported here is relevant to Case 2, which has large variance and small longitudinal correlation length. A visual comparison with the biomass distribution for Case 4 (large correlation length, not shown) revealed that the biomass growth pattern is controlled by the aspect ratio of the hydraulic conductivity field, although in a non-trivial way, and a more quantitative comparison would be difficult.

These findings raise a number of questions regarding the representativeness of samples taken in constructed wetlands with a heterogeneous substrate and regarding the quantitative understanding of the biological processes in such systems. The strong changes in biomass density in the direction transversal to the flow field suggest that use of limited sampling locations in the vertical direction is likely to be uninformative regarding the real biomass distribution. It should also be noted that in these simulations, as previously discussed, the transverse direction was neglected. However, it can be expected that the same variability observed in Fig. 6 could also be found in the transverse (horizontal) direction, since the underlying governing mechanisms are the same. This implies that, if reliable information regarding the spatial distribution of biomass (or any other component) is sought, a dense grid of sampling locations must be used to characterize each cross-section. In terms of process understanding, the results of our simulations indicate that the measured values are difficult to compare or be used as input in models. Model simulations are often calibrated or compared using the average of the measurements in a cross-section transverse to the flow direction. Since biological transformations are strongly non-linear processes – the simulation results show that the components can vary over one order of magnitude in a limited distance – it is questionable whether the use, e.g., of the arithmetic mean is the best choice to average the measurements. It should also be considered that in all the simulations reported here, while biomass growth is limited by the amount of available pore space the plugging of the pores does not affect the hydraulic properties. In other words, in heterogeneous conditions it is expected that biomass grows first in the high conductivity zones where the solutes are more quickly replaced. The growth of biomass reduces however the local hydraulic conductivity thus promoting a reduction of the heterogeneity. While this mechanism is likely, previous simulations (Brovelli et al., 2009) have shown that – at least in some conditions – clogging can further promote the increase in heterogeneity and the formation of new preferential flow paths.

To summarize, simulation results indicate that the presence of physical heterogeneities in the porous substrate induce the development of complex distribution patterns of both the mobile (solutes) and immobile components (biomass) that complicate the understanding of the processes and might reduce the overall biodegradation rate. The interactions and feedback between the different mechanisms taking place have however not been studied yet, and predictions are complicated by the non-linearity of the biological processes.

3.3 Treatment efficiency and design methodology

The results presented and discussed above indicate that heterogeneity affects the contaminant degradation rate. To gain additional insights into this aspect, we have analyzed simulation results considering the target concentrations defined in §2.3 above, namely the WHO concentration for benzene in drinking water, and the 90% removal efficiency. Results are reported in Fig. 7, where the average benzene concentrations of the 30 realizations for Cases 1 to 4 are shown as a function of the nominal HRT in the wetland, i.e., the residence time assuming that the hydraulic conductivity is constant. The results in heterogeneous conditions are compared with the simulated benzene profile obtained using a homogeneous porous medium (solid line in Fig. 7). Clearly, in all the cases with heterogeneity the two target concentrations are achieved with a longer HRT, and in some cases are not met. Recall that the values shown in Fig. 7 are the average values of the 30 realizations, meaning that for some of the realizations the target concentrations are achieved. This is important and will be further discussed in the following. In terms of design methodology, Fig. 7 can be used to identify the THRT already introduced and discussed in the methodology section. For benzene degradation considered here, the THRT for the 90% removal and WHO limit are about 2.0 d and 6.5 d (noted as $\mathrm{THRT}_{(1)}$ and $\mathrm{THRT}_{(2)}$ in Fig. 7). It is interesting to note that, due to the non-linear behavior of the microbial processes the additional benzene degradation to reach the WHO limit from the 90% degradation requires more than twice the time required to remove 90% of the initial benzene concentration.

The THRT can be used to identify the optimal inlet flow rate or the hydraulic gradient, using a tracer experiment conducted to characterize the HRTD and computing subsequently the flow velocity in the wetland's bed necessary to achieve a certain mean HRT. Furthermore, the approach we have presented is a powerful methodology to design constructed wetlands including the effect of heterogeneity. The results of the stochastic simulations are easily converted into the PFS for a given level of heterogeneity. For the setup considered in this work, the PFS is presented in Fig. 8. The panel on the left shows the PFS for 90% benzene removal, whereas the plot on the right is relevant to the WHO limit. For a given cross-section in the flow direction, the PFS is the ratio between the number of realizations for which the target concentration is achieved and the total number of realizations. The discrete values (not shown) were subsequently fitted using a logistic curve to obtain a continuous probability function. According to Fig. 8, the PFS for the setup considered in this work reaches 0 after 7 d unless the heterogeneity is large (i.e., the variance of the hydraulic conductivity is large) and the correlation length of the hydraulic conductivity field is comparable to the size of the wetland. Even in this case however, the PFS is only limited (about 20%). Since the correlation length depends primarily on the filling strategy (e.g., Suliman et al., 2007), it can in principle be controlled and reduced using an appropriate methodology during the construction phase. In other words, except for the case with large heterogeneity, the system considered would be able to remove 90% of the contaminant with a nominal

HRT of about 7 d. On the other hand, the system used here is not suitable to reach the WHO limit unless the hydraulic conductivity variability can be limited (e.g., by carefully selecting the grain size distribution of the porous material) and the correlation length minimized.

4. Summary and conclusions

The effect of the porous medium physical heterogeneity on the HRTD of horizontal subsurface flow constructed wetlands and sand filters was analyzed by means of numerical simulations. Heterogeneity was included in the simulated domain using random spatially correlated hydraulic conductivity fields. The extent of heterogeneity was controlled by the variance of the hydraulic conductivity distribution and by the correlation length in the flow direction. It was observed that substrate heterogeneity induces preferential flow paths, modifies the HRTD and results in variations of the treatment efficiency. Simulated tracer tests conducted to characterize the residence time distribution showed that as the extent of the heterogeneity increases (increase in variance and longitudinal correlation length similar to the size of system) the mean HRT decreases, the HRTD becomes broader and its skewness increases. Moreover, scale-dependent behavior was observed: The sensitivity of the HRTD to heterogeneity was larger when the correlation length was comparable to the dimensions of the system. In other words, if the system is large compared to the scale at which the hydraulic conductivity varies the effect of heterogeneity is limited. Similar observations were made regarding the effect of heterogeneity on the removal rate. Furthermore, and possibly more important, it was found that the microbial growth patterns are affected by the flow field, and that as heterogeneity increases the biomass spatial distribution becomes more complex and the removal rate shows larger variability (as shown by the increase in the standard deviation in Fig. 5). These insights on the biomass distribution indicate that collection of a limited number of samples in the transverse directions is of limited use because the representativeness of few samples is small.

The approach presented in this work is a possible design methodology for constructed wetlands, in that the effect of heterogeneity can be incorporated in a quantitative manner. The methodology is based on the use of numerical tools to simulate solute transport and biodegradation, and therefore requires knowledge of the processes involved, including their parameterization. On the other hand, a process-based design can prove extremely helpful in reducing the sources of uncertainty, therefore improving the treatment efficiency and reliability of the system. In this respect, detailed mechanistic simulators are of increased importance. The key advantage of the approach is that it uses a stochastic methodology to evaluate the effect of heterogeneity on removal rate and the HRTD. For a given configuration of the wetland, multiple realizations of statistically equivalent hydraulic conductivity random fields are generated. This is a standard technique used in subsurface hydrology, and its application to CWs is straightforward. This approach allows the computation of the probability of failure of the system as a function of the HRT. The optimal dimension of the system can subsequently be decided based on the expected flow rate, its variations and the probability of failure that can be tolerated. For example, if the water body receiving the water discharged from the treatment plant is very sensitive, a low probability of failure is required even for the maximum expected loading rate of the system, and the system must be dimensioned accordingly. Although the approach presented in this work makes use of tools that might not common in the constructed wetland community, it should be clear that they are available and their diffusion and use might be extremely beneficial to overcome some of the major limitations of CWs. Moreover, it is important to note that this same methodology can be further extended to incorporate additional sources of variability and uncertainty, for example those affecting the degradation rates of the contaminants (temperature, loading rate, etc.), therefore making the design phase more reliable and effectively process-based. In other words, every aspect showing some level of stochastic variability can be modeled within the same framework, given that the statistical properties of the random process are known. However, to be able to extend the method in this direction, the use of more sophisticated simulators is required and therefore more research is required.

References

Akratos, C.S., Tsihrintzis, V.A., 2007. Effect of temperature, HRT, vegetation and porous media on removal efficiency of pilot-scale horizontal subsurface flow constructed wetlands. Ecol. Eng. 29 (2), 173–191.

Alagappan, G., Cowan, R.M., 2004. Effect of temperature and dissolved oxygen on the growth kinetics of Pseudomonas putida F1 growing on benzene and toluene. Chemosphere 54 (8), 1255–1265.

Ascuntar-Rios, D., Toro-Vélez, A.F., Peña, M.R., Madera-Parra, C.A., 2009. Changes of flow patterns in a horizontal subsurface flow constructed wetlands treating domestic wastewater in tropical regions. Ecol. Eng. 35 (2), 274–280.

Bajracharya, K., Barry, D.A., 1997. Nonequilibrium solute transport parameters and their physical significance: Numerical and experimental results. J. Contam. Hydrol. 24 (3-4), 185–204.

Barnett, V., O'Hagan, A. 1997. Setting environmental standards: the statistical approach to handling uncertainty and variation. Chapman & Hall, London, p. 112.

Barry, D.A., 1990. Supercomputers and their use in modeling subsurface solute transport. Rev. Geophys., 28 (3), 277–295.

Barry, D.A., Coves, J., Sposito, G., 1988. On the Dagan model of solute transport in groundwater: Application to the Borden site. Water Resour. Res., 24 (10), 1805–1817.

Barry, D.A., Prommer, H., Miller, C.T., Engesgaard, P., Brun, A., Zheng, C., 2002. Modelling the fate of oxidisable organic contaminants in groundwater. Adv. Water Resour., 25 (8-12), 945–983.

Barry, D.A., Sposito, G., 1988. Application of the convection-dispersion model to solute transport in finite soil columns. Soil Sci. Soc. Am. J., 52 (1), 3–9.

Barry, D.A., Sposito, G., 1990. Three-dimensional statistical moment analysis of the Stanford/Waterloo Borden tracer data. Water Resour. Res., 26 (8), 1735–1747.

Bear, J., Verruijt, A., 1986. Modeling groundwater flow and pollution, with computer programs for sample cases, D. Reidel Publ. Co., Dordrecht, Germany, p. 414.

Bedessem, M.E., Ferro, A.M., Hiegel, T., 2007. Pilot-scale constructed wetlands for petroleum-contaminated groundwater. Water Environment Research 79, 581–586. Brix, H., Arias, C.A., 2005. Danish guidelines for small-scale constructed wetland systems for onsite treatment of domestic sewage. Water Sci. Technol. 15 (9), 1–9.

Brovelli, A., Malaguerra, F., Barry, D.A., 2009. Bioclogging in porous media: Model development and sensitivity to initial conditions. Environ. Model. Softw. 24 (5), 611–626.

Caselles-Osorio, A., García, J., 2006. Performance of experimental horizontal subsurface flow constructed wetlands fed with dissolved or particulate organic matter. Water Res. 40 (19), 3603–3611.

Chazarenk, F., Merlin, G., Gonthier, Y., 2003. Hydrodynamics of horizontal subsurface flow constructed wetlands. Ecol. Eng. 21 (2-3), 165–173.

Chiang, W.H., 2005. 3D groundwater modeling with PMWIN, 2nd ed. Springer-Verlag, The Netherlands, p. 397.

Chin, D.A., 2006. Water quality engineering in natural systems. Wiley-Interscience, NJ, USA, p. 610.

Coats, K.H., Smith, B.D., 1964. Dead-end pore volume and dispersion in porous media. Soc. Petrol. Eng. J., 4 (3), 73–84.

Dagan, G., 1984. Solute transport in heterogeneous porous formations. J. Fluid Mech., 145, 151–177.

Dagan, G., 1989. Flow and Transport in Porous Formations, Springer-Verlag, Berlin, Germany. p. 465.

Dittmer, U., Meyer, D., Langergraber, G., 2005. Simulation of a subsurface vertical flow constructed wetland for CSO treatment. Water Sci Technol 51(9), 225–232.

Eke, P.E., Scholz, M., 2008. Benzene removal with vertical-flow constructed treatment wetlands. Journal of Chemical Technology and Biotechnology 83, 55–63.

Frenzel, H., 1995. A field generator based on Mejia's algorithm. Institut für Umweltphysik, University of Heidelberg, Germany.

García, J., Chiva, J., Aguirre, P., Álvarez, E., Sierra, J.P., Mujeriego, R., 2004. Hydraulic behavior of horizontal subsurface flow constructed wetlands with different aspect ratio and granular medium size. Ecol. Eng., 23 (3), 177−187.

Gelhar, L.W., Welty C., Rehfeldt K.R., 1992. A critical review of data on field-scale dispersion in aquifers. Water Resour. Res., 28 (7), 1955–1974.

Giraldi, D., de Michieli Vitturi, M., Iannelli, R., 2010. FITOVERT: A dynamic numerical model of subsurface vertical flow constructed wetlands. Environ. Model. Software. 25 (5), 633–640.Gödeke, S., Vogt, C., Schirmer, M., 2008. Estimation of kinetic Monod parameters for anaerobic degradation of benzene in groundwater. Environ. Geol., 55 (2), 423–431.

Griffioen, J.W., Barry, D.A., Parlange. J.-Y., 1998. Interpretation of two-region model parameters. Water Resour. Res., 34 (3), 373–384.

Grismer, M.E., Tausendschoen, M., Shepherd, H., 2001. Hydraulic characteristics of a subsurface flow constructed wetland for winery effluent treatment. Water Environ. Res., 73 (4), 466–477.

Haberl, R., Grego, S., Langergraber, G., Kadlec, R.H., Cicalini, A.R., Dias, S.M., Novais, J.M., Gerth, A., Thomas, H., Hebner, A., 2003. Constructed wetlands for treatment of organic pollutants. J. Soils Sediments, 3 (2), 109–124.

Hamed, M.M., Bedient, P.B., Dawson, C.N., 1996. Probabilistic modeling of aquifer heterogeneity using reliability methods. Adv. Water Resour., 19 (5), 277–295.

Hench, K.R., Bissonnette, G.K., Sexstone, A.J., Coleman, J.G., Garbutt, K., Skousen, F.G., 2003. Fate of physical, chemical, and microbial contaminants in domestic wastewater following treatment by small constructed wetlands. Water Res., 37 (4), 921‒927.

Hristopulos, D.T., 2003. Renormalization group methods in subsurface hydrology: Overview and applications in hydraulic conductivity upscaling. Adv. Water Resour., 26 (12), 1279–1308.

Imfeld, G., Braeckvelt, M., Kuschk, P., Richnow, H., 2009. Monitoring and assessing processes of organic chemicals removal in constructed wetlands. Chemosphere, 74 (3) 349–362.

Jenkins, G.A., Greenway, M., 2005. The hydraulic efficiency of fringing versus banded vegetation in constructed wetlands. Ecol. Eng., 25(1), 61–72.

Johnson, S.J., Woolhouse, K.J., Prommer, H., Barry, D.A., Christofi. N., 2003. Contribution of anaerobic microbial activity to natural attenuation of benzene in groundwater. Eng. Geol., 70 (3-4), 343–349.

Kadlec, R.H. 1997. Deterministic and stochastic aspects of constructed wetland performance and design. Water Sci. Technol., 35(5), 149–159.

Kadlec, R.H., 2003. Effects of pollutant speciation in treatment wetlands design. Ecol. Eng., 20 (1), 1–16.

Kadlec, R.H., 2009. Comparison of free water and horizontal subsurface treatment wetlands. Ecol. Eng., 35 (2), 159–174.

Kadlec, R.H., Wallace, S.D., 2009. Treatment Wetlands, 2nd ed. CRC Press, Boca Raton, FL, USA, p. 1016.

Kamra, S.K., Lennartz, B., van Genuchten, M.Th., Widmoser, P., 2001. Evaluating non-equilibrium solute transport in small soil columns. J. Contam. Hydrol., 48 (3-4), 189–212.

King, A.C., Mitchell, C.A., Howes, T., 1997. Hydraulic tracer studies in a pilot scale subsurface flow constructed wetland. Water Sci. Technol., 35(5), 189–196.

Kjellin, J., Wörman, A., Johansson, H., Lindahl, A., 2007. Controlling factors for water residence time and flow patterns in Ekeby treatment wetland, Sweden. Adv. Water Resour., 30 (4), 838–850.

Knowles, P.R., Griffin, P., Davies, P.A., 2008. An investigation into the development of heterogeneous hydraulic conductivity profiles in constructed wetlands for wastewater treatment. 11th International Conference on Wetland Systems for Water Pollution Control IWA. Indore, India. pp. 814–824.

Kottegoda, N.T., Katuuk, G.C., 1983. Effect of spatial variation in hydraulic conductivity on groundwater flow by alternate solution techniques. J. Hydrol., 65 (4), 349–362.

Kreft, A., Zuber, A., 1978. On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions. Chem. Eng. Sci., 33 (11), 1471–1480.

Langergraber, G., 2003. Simulation of subsurface flow constructed wetlands- Results and further research needs. Water Sci. Technol. 48, 157–166.

Langergraber, G., 2007. Simulation of the treatment performance of outdoor subsurface flow constructed wetlands in temperate climates. Sci. Total Environ. 380, 210–219.

Langergraber, G., 2008. Modeling of processes in subsurface flow constructed wetlands: A review. Vadose Zone Journal. 7, 830–842.

Langergraber, G., Giraldi, D., Mena, J., Meyer, D., Peña, M., Toscano, A., Brovelli, A., Korkusuz, E.A., 2009a. Recent developments in numerical modelling of subsurface flow constructed wetlands. Sci. Total Environ., 407 (13), 3931–3943.

Langergraber, G., Rousseau, D.P., Garcia, J., Mena, J., 2009b. CWM1: a general model to describe biokinetic processes in subsurface flow constructed wetlands. Water Sci. Technol. 59, 1687–1697.

Leverenz, H.L., Tchobanoglous, G., Darby, J.L., 2009. Clogging in intermittently dosed sand filters used for wastewater treatment. Water Res., 43 (3), 695–705.

Lewis, M.E., 2006. Dissolved oxygen. U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6.

Li, L., Barry, D.A., Stone, K.J.L., 1994. Centrifugal modelling of nonsorbing, nonequilibrium solute transport in a locally inhomogeneous soil. Canad. Geotech. J., 31 (4), 471–477.

Lin, T., Wen, Y., Jiang, L., Li, J., Yang, S., Zhou, Q., 2008. Study of atrazine degradation in subsurface flow constructed wetland under different salinity. Chemosphere, 72 (1), 122–128.

McDonald, M., Harbaugh, A., 1988. A Modular Three-Dimensional Finite-Difference Ground-Water Flow Model. U.S Geological Survey, USA.

Małoszewski, P., Wachniew, P., Czuprynski, P., 2006. Study of hydraulic parameters in heterogeneous gravel beds: Constructed wetland in Nowa Slupia (Poland). J. Contam. Hydrol., 331 (3-4), 630–642.

Mao, X., Prommer, H., Barry, D.A., Langevin, C., Panteleit, B. 2006. Three-dimensional model for multi-component reactive transport with variable density groundwater flow. Environ. Model. Softw., 21 (5), 615–628.

Marsili-Libelli, S., Checchi, N., 2005. Identification of dynamic models for horizontal subsurface constructed wetlands. Ecol. Model., 187, 201–218.

Matamoros, V., Bayona, J.M., 2006. Elimination of pharmaceutical and personal care products in subsurface flow constructed wetlands. Environ. Sci. Technol., 40 (18), 5811–5816.Matamoros, V., Puigagut, J., García, J., Bayona, J.M., 2007a. Behavior of selected priority organic pollutants in horizontal subsurface flow constructed wetlands: A preliminary screening. Chemosphere, 69 (9), 1374–1380.

Mayo, A.W., Bigambo, T., 2005. Nitrogen transformation in horizontal subsurface flow constructed wetlands I: Model development. Physics and Chemistry of the Earth. 30, 658–667.

Matamoros, V., Arias, C., Brix, H., Bayona, J.M., 2007b. Removal of pharmaceuticals and personal care products (PPCPs) from urban wastewater in a pilot vertical flow constructed wetland and a sand filter. Environ. Sci. Technol., 41 (23), 8171−8177.

Matamoros, V., García, J., Bayona, J.M., 2008. Organic micropollutant removal in a full-scale surface flow constructed wetland fed with secondary effluent. Water Res., 42 (3), 653–660.

McGechan, M.B., Moir, S.E., Castle, K., Smit, I.P.J., 2005. Modelling oxygen transport in a reedbed-constructed wetland purification system for dilute effluents. Biosyst. Engin. 91, 191–200.

Mejia J.M., Rodriguez-Iturbe I., 1974. On the synthesis of random field sampling from the spectrum: An application to the generation of hydrologic spatial processes. Water Resour. Res., 10 (4), 705–711.

Mena, J., Gómez, R., Villaseñor, J., De-Lucas, A., 2008. Operation time influence on constructed wetlands hydraulic. 11th International Conference on Wetland Systems for Water Pollution Control IWA. Indore, India, p. 445.

Moore, B.J., Lyness, L.S., Ross, S.D., Armstrong, J.E., Bowles, M.W., 2000. Innovative approaches for the remediation of petroleum hydrocarbons in groundwater, 16th World Petroleum Congress, Calgary, Canada, pp. 46–48.

Muñoz, P., Drizo A., Hession, C., 2006. Flow patterns of dairy wastewater constructed wetlands in a cold climate. Water Res., 40 (17), 3209–3218.

OEaux, 2008. Swiss Federal Ordinance for water protection (In French, Ordonnance sur la protection des eaux), RS 814.201, Swiss legislation, Bern, Switzerland.

Orhon, D., Artan, N., 1994. Modelling of activated sludge systems. Technomic Publishing Company, Inc., Lancaster, Pennsylvania, USA, p. 589.

Parker J.C., van Genuchten M.Th., 1984. Flux-averaged and volume-averaged concentrations in continuum approaches to solute transport. Water Resour. Res., 20 (7), 866–872.

Parlange, J.-Y., Barry, D.A., Starr, J.L., 1985. Comments on "Boundary conditions for displacement experiments through short laboratory soil columns". Soil Sci. Soc. Am. J., 49 (5), 1325.

Parlange, J.-Y., Starr, J.L., van Genuchten, M.Th., Barry, D.A., Parker, J.C., 1992. Exit condition for miscible displacement experiments. Soil Sci., 153 (3), 165–171.

Persson, J., Somes, N.L.G., Wong, T.H.F., 1999. Hydraulic efficiency of constructed wetlands and ponds. Water Sci. Technol., 40 (3), 291–300.

Prommer, H., Barry, D.A., 2005. Modeling bioremediation of contaminated groundwater. In: Atlas, R., Philip, J.C. (Eds.), Bioremediation: Applied microbial solutions for real-world environmental clean-up, pp. 108–138. AMS Press, American Society for Microbiology. Washington, DC, USA.

Prommer, H., Barry, D.A., Davis, G.B., 1999. A one-dimensional reactive multi-component transport model for biodegradation of petroleum hydrocarbons in groundwater. Environ. Model. Softw., 14 (2-3), 213–223.

Prommer, H., Barry, D.A., Davis, G.B., 2000. Numerical modelling for design and evaluation of groundwater remediation schemes. Ecol. Model., 128 (2-3), 181–195.

Rash, J.K., Liehr, S.K., 1999. Flow pattern analysis of constructed wetlands treating landfill leachate. Water Sci. Technol., 40 (3), 309–315.

Reiche, N., Lorenz, W., Borsdorf, H., 2010. Development and application of dynamic air chambers for measurement of volatilization fluxes of benzene and MTBE from constructed wetlands planted with common reed. Chemosphere 79, 162–168.Reinoso, R., Torres, L.A., Bécares, E., 2008. Efficiency of natural systems for removal of bacteria and pathogenic parasites from wastewater. Sci. Total Environ., 395 (2-3), 80–86.

Robinson, C., Brovelli, A., Barry, D.A., Li, L., 2009. Tidal influence on BTEX biodegradation in sandy coastal aquifers. Adv. Water Resour., 32 (1), 16–28.

Rossi L., Chèvre N., Fankhauser R., Krejci V. (2009) Probabilistic environmental risk assessment of urban wet-weather discharges: an approach developed for Switzerland. Urban Water J., 6 (5), 355–367.

Rousseau, D.P.L., Vanrolleghem, P.A., De Pauw, N., 2004. Model-based design of horizontal subsurface flow constructed treatment wetlands: A review. Water Res., 38 (6), 1484–1493

Schirmer, M., Molson, J.W., Frind, E.O., Barker, J.F., 2000. Biodegradation modelling of a dissolved gasoline plume applying independent laboratory and field parameters. J. Contam. Hydrol., 46, 339–374.

Skaggs, T. H., Barry, D.A., 1997. The first-order reliability method of predicting cumulative mass flux in heterogeneous porous formations. Water Resour. Res., 33 (6), 1485–1494.

Sposito, G., Barry, D.A., 1987. On the Dagan model of solute transport in groundwater: Foundational aspects. Water Resour. Res., 23 (10), 1867–1875.

Stott, R., Warren, A., Williams, J., Ramirez, E., 2008. The removal of pathogens and parasites in sub-surface flow constructed wetlands treating wastewaters in Egypt, Mexico and the UK. 11th International Conference on Wetland Systems for Water Pollution Control IWA. Indore, India, p. 782.

Suliman, F., Futsaether, C., Oxaal, U., 2007. Hydraulic performance of horizontal subsurface flow constructed wetlands for different strategies of filling the filter medium into the filter basin. Ecol. Eng., 29 (1), 45−55.

Suliman, F. Futsaether, C., Oxaal, U., Haugen L.E., Jenssen, P., 2006a. Effect of inlet-outlet positions on the hydraulic performance of horizontal subsurface-flow wetlands constructed with heterogeneous porous media. J. Contam. Hydrol., 87 (1-2), 22–36.

Suliman, F., French, H.K., Haugen, L.E., Sovik, A.K., 2006b. Change in flow and transport patterns in horizontal subsurface flow constructed wetlands as a result of biological growth. Ecol. Eng., 27 (2), 124–133.

Suliman, F., French, H., Haugen, L.E., Klove, B., Jenssen, P., 2005. The effect of the scale of horizontal subsurface flow constructed wetlands on flow and transport parameters. Water Sci. Technol., 51 (9), 259–266.

Tang, X., Eke, P.E., Scholz, M., Huang, S., 2008. Processes impacting on benzene removal in vertical-flow constructed wetlands. Bioresource Technology 100, 227–234.

Tang, X., Eke, P.E., Scholz, M., Huang, S., 2009. Seasonal variability in benzene removal by vertical-flow constructed wetland filters. Water, Air, and Soil Pollution 202, 259–272.

Toscano, A., Langergraber, G., Consoli, S., Cirelli, G.L., 2009. Modelling pollutant removal in a pilot-scale two-stage subsurface flow constructed wetlands. Ecol. Eng. 35, 281–289.

van Genuchten, M.Th., Parker, J.C., 1984. Boundary conditions for displacement experiments through short laboratory soil columns. Soil Sci. Soc. Am. J., 48 (4), 703–708.

Vymazal, J., 2007. Removal of nutrients in various types of constructed wetlands. Sci. Total Environ., 380 (1-3), 48–65.

Vymazal, J., Kröpfelová, L., 2008. Wastewater treatment in constructed wetlands with horizontal sub-surface flow. Series Environmental Pollution, vol 14. Springer-Verlag, The Netherlands, p. 566.

Wallace, S., Kadlec, R., 2005. BTEX degradation in cold-climate wetland system. Water Sci. Technol., 51 (9), 165–171.

Wallace, S.D., 2001. On-site remediation of petroleum contact wastes using subsurface flow wetlands. Procs 2nd int. conf. wetlands and remediation. Vermont, USA.

World Health Organization. Guidelines for drinking-water quality, vol. 1, recommendations 2006.

Wörman, A., Kronnäs, V., 2005. Effect of pond shape and vegetation heterogeneity on flow and treatment performance of constructed wetlands. J. Hydrol., 301, 123–138

Wynn, T.M., Liehr, S.K., 2001. Development of a constructed subsurface-flow wetland simulation model. Ecol. Eng., 16 (4), 519–536.

Zheng, C., Wang, P., 1999. MT3DMS, a Modular Three-Dimensional Multi-Species Transport Model for Simulation of Advection, Dispersion and Chemical Reactions of Contaminants in Ground-Water Systems; Documentation and User's Guide. U.S. Army Engineer Research and Development Center, USA.

Tables

Table 1. Main features of the constructed wetland model. Typical values for subsurface flow constructed wetlands for secondary treatment were used (e.g., Brix and Arias, 2005; Chin, 2006; Kadlec and Wallace, 2009). The hydraulic conductivity listed in this table is relevant to the case with homogenous porous medium.

Property	**Value**	**Units**
Length	10	m
Depth	1	m
Nominal residence time(a)	9.5	d
Porosity	0.38	-
Hydraulic conductivity(b)	20	$m\ d^{-1}$
Hydraulic gradient	2×10^{-2}	-
Longitudinal dispersivity	2×10^{-2}	m

(a)Based on the expected seepage velocity and the size of the system

(b)The same value was used for both vertical and horizontal hydraulic conductivity

Table 2. Stoichiometry and Monod kinetic parameters for the aerobic degradation of benzene. Also listed are the influent concentrations of benzene and oxygen, and the initial biomass concentration.

Parameter	Value	Units	Source
$\mu_{max,B}$	1	d^{-1}	Average value$^{(a)}$
$K_{S,B}$	3×10^{-2}	mmol l^{-1}	Alagappan and Cowan (2004)
Y_b	6×10^{-1}	-	Alagappan and Cowan (2004)
$K_{S,O}$	3.6×10^{-2}	mmol l^{-1}	Alagappan and Cowan (2004)
S_B	7.5	(mol O_2)(mol C_6H_6)$^{-1}$	Stoichiometry, Eq. (1)
k_d	10^{-3}	d^{-1}	Assumed$^{(b)}$
Benzene$^{(c)}$	3.5×10^{-2}	mmol l^{-1}	Assumed
Oxygen$^{(c)}$	28.7×10^{-2}	mmol l^{-1}	Solubility limit at 20°C (Lewis, 2006)
Biomass$^{(c)}$	3×10^{-2}	mmol l^{-1}	Assumed
X_b^{max}	2	mmol l^{-1}	Computed using literature value$^{(d)}$

(a) From Schirmer et al. (2000) and Gödeke et al. (2008).

(b) A small value is used for the first-order biomass decay rate because in reality microbial growth is supported by alternative carbon and energy sources, which are not included in the model

(c) Influent concentration

(d) Orhon and Artan (1994); Brovelli et al. (2009).

Table 3. Summary of the properties of the hydraulic conductivity fields in the four cases discussed in the text, as well as the homogeneous case. The effective (bulk) hydraulic conductivity K is the average (±1 standard deviation) of the 30 realizations.

Case	**Hydraulic conductivity**(a)		**Correlation length (m)**		**Effective K** $(m\ d^{-1})$
	Mean value *$(m\ d^{-1})$*	*Variance* *$(m^2\ d^{-2})$*	*Longitudinal*	*Vertical*	
H(b)	20	-	-	-	20
1	20	4	1	0.15	22.05 ± 0.64
2	20	16	1	0.15	27.62 ± 3.77
3	20	4	8	0.15	24.59 ± 0.60
4	20	16	8	0.15	50.72 ± 6.63

(a)Parameters of the log-normal distribution (base 10)

(b)Homogeneous (base) case. The hydraulic conductivity is constant

Figures

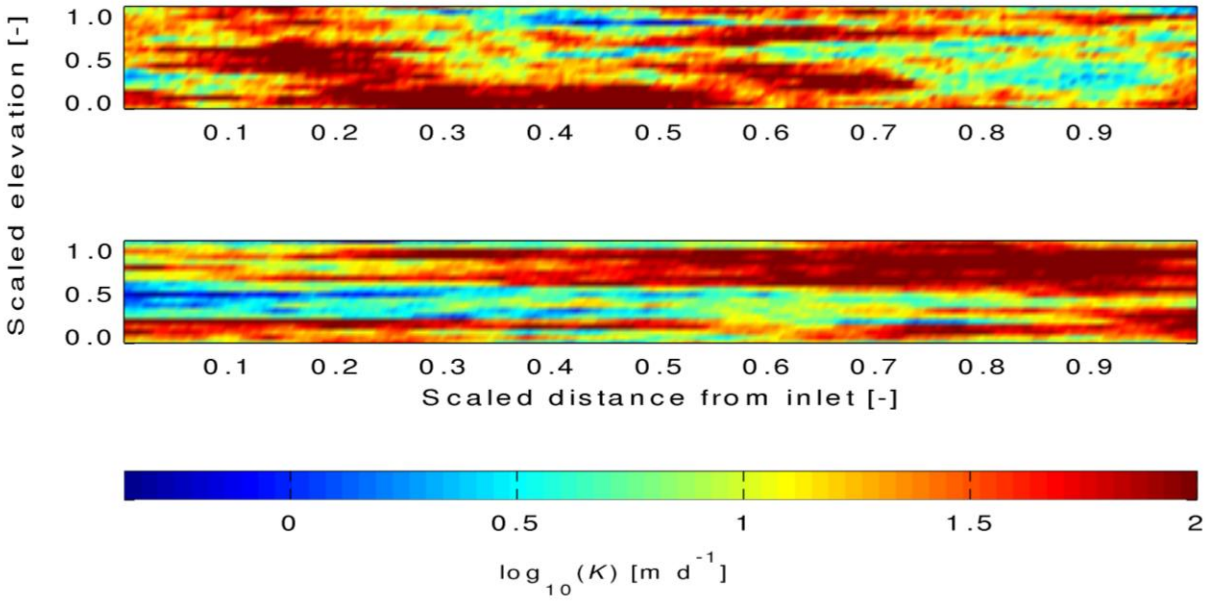

Figure 1. Example of heterogeneous hydraulic conductivity random fields used in the simulations. The mean, the variance and the vertical correlation length are the same in the two panels. The *x* and *y* axes are scaled by the real dimensions. The longitudinal correlation length is small compared to model size in the top panel, while is comparable to the dimension of the system in the bottom panel, leading to a vertically stratified system (e.g., Sposito and Barry, 1987).

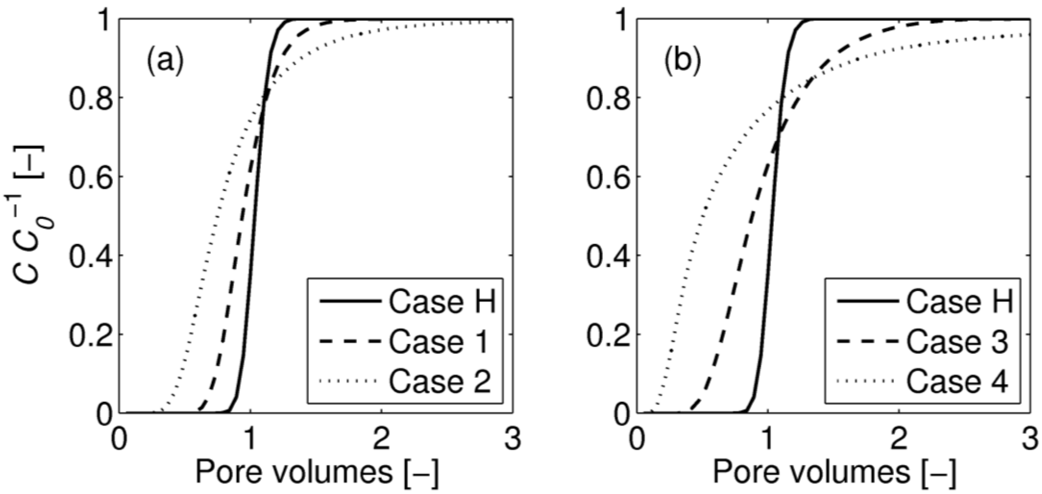

Figure 2. Simulated BTCs of the conservative tracer with homogenous (Case H, solid line) and heterogeneous (broken lines) porous media. The average breakthrough of 30 realizations is shown. On the left panel (a) the homogeneous case is compared with cases 1 and 2, while on the right panel (b) the BTCs for cases 3 and 4 are reported (see Table 3 for details regarding the statistical properties of the conductivity fields). The simulation results indicate that heterogeneity modifies the HRTD. The mean HRT decreases while the spreading is accentuated. This indicates that hydraulic conditions are less favorable for degradation then the homogeneous case.

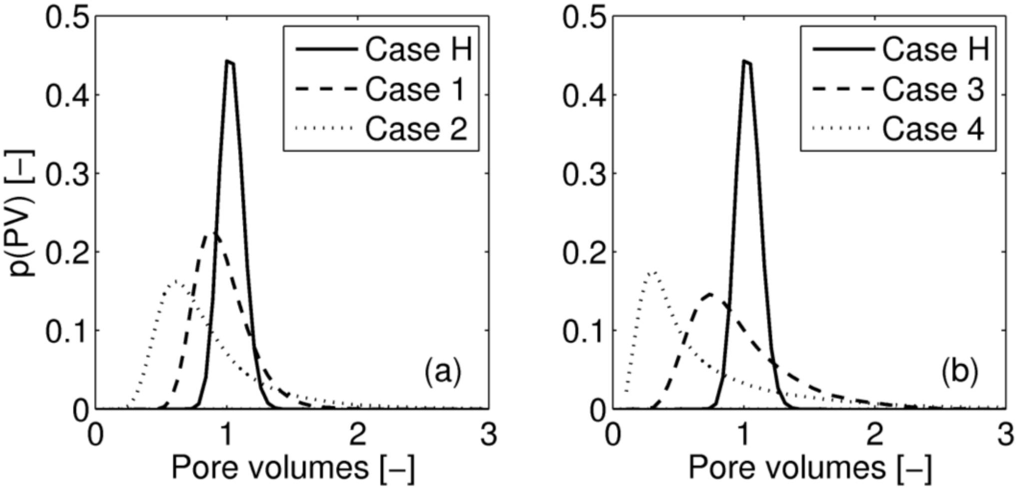

Figure 3. HRTDs for the simulations with constant hydraulic conductivity (solid line) and with spatially variable hydraulic properties (broken lines). Panels (a) and (b) show the results for short and long correlation lengths, respectively. The HRTD is sharp and symmetric with the peak corresponding to the nominal retention time (one pore volume) only for the homogeneous case. Increasing the variance and the correlation length of the conductivity field leads to a reduction in the mean HRT while both the variance and skewness of the HRTD increase.

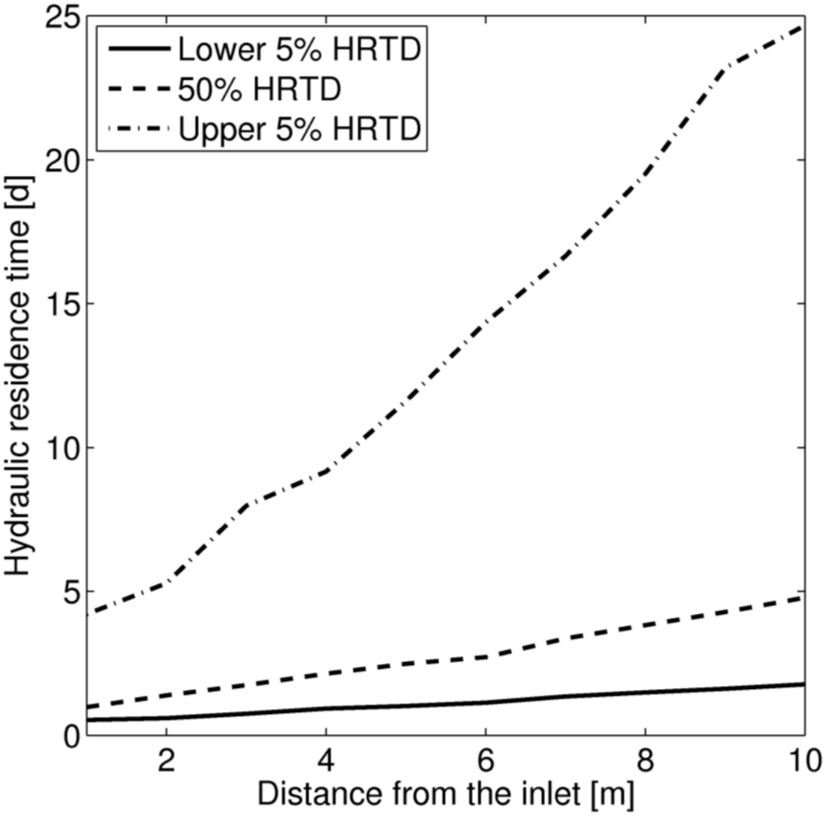

Figure 4. Evolution of HRTD as function of the distance from the inlet for the worst case (i.e., large variance and correlation length, Case 4). For a wetland of length of, say, 4 m, the dashed line indicates that, of the solute flowing through the system, 95% will experience an HRT of, approximately, at least 1 d, 50% at least 2 d and 5% at least 9 d. Despite the large heterogeneity, the evolution of the mean HRT (50% mass has passed a given location), as well as that of the upper and lower 0.05 percentiles can be considered linear.

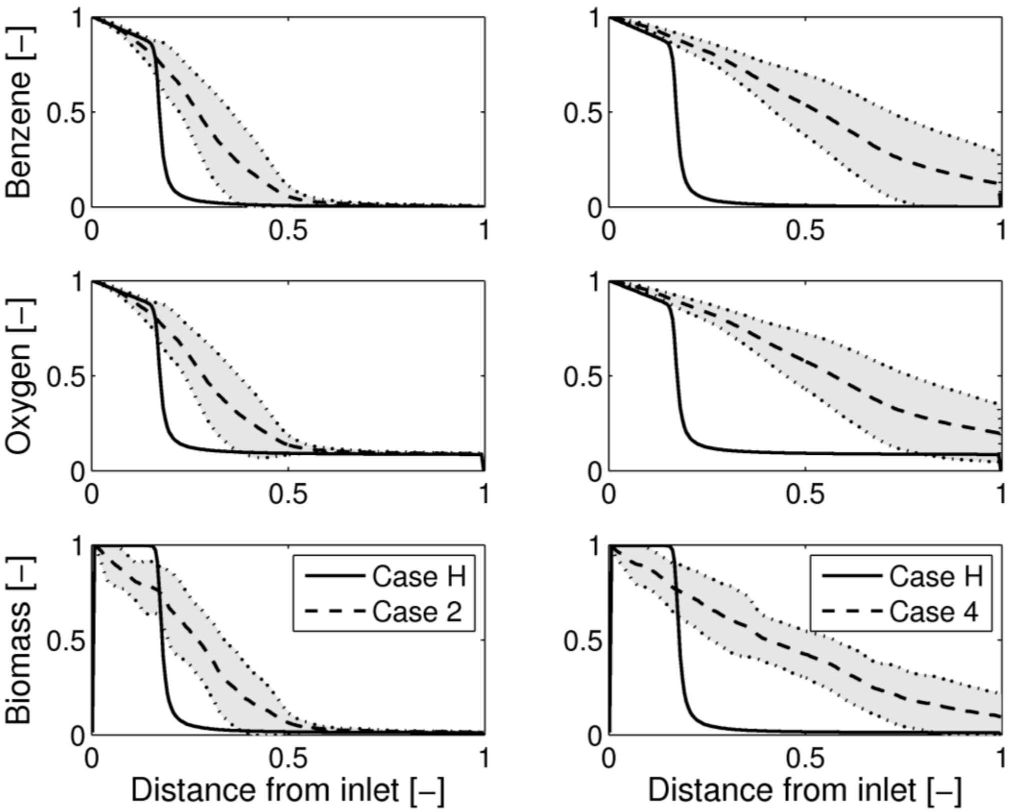

Figure 5. Normalized benzene, oxygen and biomass distributions in the homogeneous case (Case H) and in the two cases with larger variance of the hydraulic conductivity distribution (Cases 2 and 4, Table 3). The *x* axis is scaled by the longitudinal dimension of the simulated wetland. The dashed line shows the average value for the 30 realizations while the area shaded in gray indicates ±1 standard deviation. These results confirm that physical heterogeneity influences the biological processes and reduces the contaminant removal efficiency.

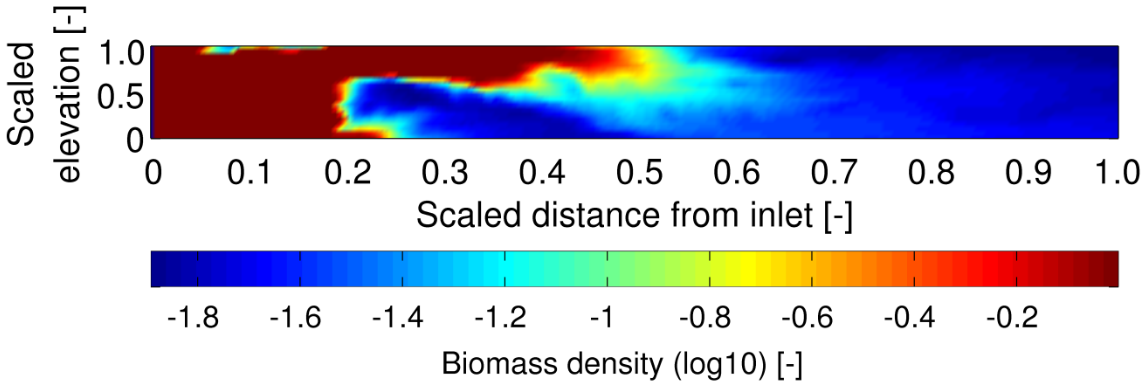

Figure 6. Example of simulated biomass distribution with heterogeneous hydraulic conductivity (Case 2, large variance and short correlation length). The biomass pattern shows spatial variability due to the irregular distribution of the flow and of the contaminants. This indicates that local measurements of biomass are poorly representative of the real biomass density and distribution in heterogeneous systems.

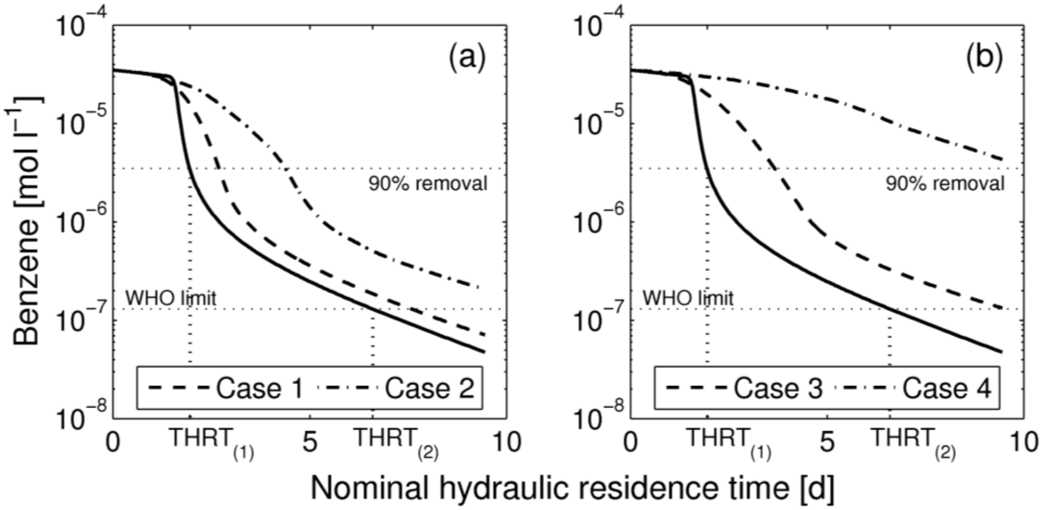

Figure 7. Simulated benzene degradation in homogeneous and heterogeneous conditions. In cases 1 and 2 (panel (a), left) the longitudinal correlation length is small (0.1 of the length of the simulated system) whereas for panel (b) the longitudinal correlation length is comparable to the wetland's length. $\text{THRT}_{(1)}$ and $\text{THRT}_{(2)}$ indicate the target hydraulic residence time required to achieve the two metrics. Results for the homogeneous case (solid line) are presented for comparison. In all cases with heterogeneity the removal rate is smaller than in the homogeneous case. The variance of the hydraulic conductivity distribution has the larger effect on the removal rate, which however also decreases as the correlation length increases.

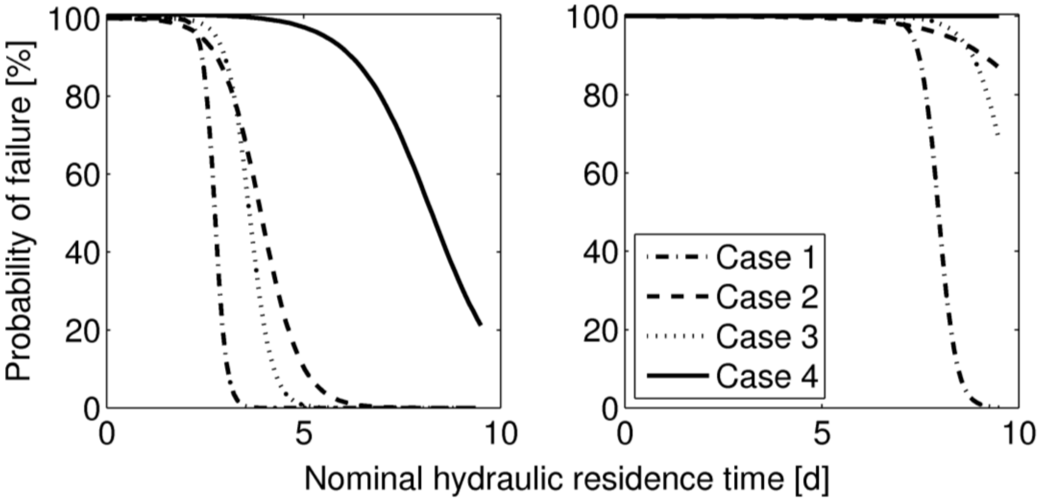

Figure 8. PFS as a function of the nominal HRT (computed assuming homogeneous conditions). The left panel reports the PFS of the four heterogeneous cases for the target concentration corresponding to 90% removal efficiency, while the right panel (b) is relevant to WHO limit for drinking water. Although in the first case the HRT is large enough to guarantee that the target concentration is met in most of the studied conditions, for the WHO limit our methodology predicts that the system will most likely fail and a longer HRT is necessary.