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Modelling the long-term accumulation and migration of heavy metals in Sustainable Urban Drainage Systems: a sensitivity analysis

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Abstract
The increasing use of SUDS for stormwater management raises some concerns about the fate of ubiquitous runoff contaminants in soils and their potential threat to groundwater. A reactive transport model may be a valuable tool to assess their long-term behaviour in these systems and derive guidelines about the conception and maintenance of such devices, but so far, very few modelling studies have been undertaken in this particular context. This paper presents several modelling options and corresponding hypotheses, and discusses their application to a theoretical "source control" technique.
The inter-event variability of a pollutant's mean concentration in runoff affects the sorbed concentration in the first centimetres of soil, and slightly influences its global migration dynamics. The shape of the sorption isotherm (linear, Langmuir of Freundlich models) induces noticeable differences in the predicted contamination profiles. Given the typical time constants of sorption processes, taking into account rate-limited mechanisms causes differences in solute concentrations lower than 4% of the concentration in runoff, and this difference decreases with increasing inflow rate and dispersivity of the soil. The latter parameter was found to have a significant effect on both contaminant profiles and fluxes, but experimental studies show that it may vary within more than two orders of magnitude, and that laboratory-scale measurements tend to underestimate the *in-situ* values. The uncertainty in the contamination patterns caused by a biased estimation of the dispersion parameter is likely to be larger than the accuracy gained with a more complex modelling framework.

Keywords
Contaminant transport, Heavy metals, Modelling, Soil, Source control techniques, SUDS

INTRODUCTION

Sustainable Urban Drainage Systems (SUDS) are becoming a widespread approach for stormwater management in a context of urban sprawl and rising levels of impervious cover, because of their largely recognised hydraulic and hydrologic benefits. Their implementation helps to mitigate increases in both the peak rate and total volume of runoff caused by land development, reduce combined sewer overflows to receiving water, and contribute to groundwater replenishment (Dechesne, et al., 2004; Davis, et al., 2009). Among these practices, the use of infiltration facilities – when hydraulic conductivity enables it – induces some concerns about the fate of contaminants within these devices, and their potential impact on soil and groundwater. The ubiquitous nature of several micropollutants in urban frameworks (*e.g.* heavy metals (HM) and polycyclic aromatic hydrocarbons), the concentrations likely to be found in runoff, and their mostly conservative behaviour in soils, raises two main uncertainties: (*i*) potential for nonpoint source contamination of soils, and possible needs for cleaning-up after several years of operation; (*ii*) risks of contaminant

transport to groundwater. Experimental studies may give insight into the former point; however, assessing the long-term fate and transport of pollutants and quantifying the amount reaching the water table require the use of a reactive transport model.

In this paper, we focus on "source control" techniques, such as swales, rain gardens or small infiltration basins, in which the fate and transport of contaminants (accumulation, degradation, remobilization, transfer) somewhat suffers from a lack of documentation. Even if a wide variety of models are available to describe solute and/or particulate transport in porous media (Simunek, et al., 2003), so far, very few modelling studies have been undertaken in the specific context of SUDS, and the chemical species to which these models have been applied are only HM or non-reactive tracers. The objective was either to simulate concentration patterns measured in a study site, or to perform a sensitivity analysis on given parameters, considering a generic device.

It should be noticed that the modelling framework was very different from one study to another. For example, Li and Davis (2008) used the analytical solutions of the equation describing one-dimensional contaminant transport, which requires strong simplifying assumptions about the modelled soil (fully-saturated, semi-infinite media, with a constant upper water flux), but considered a vertical distribution of suspended solids in soil; Winiarski et al. (2013) and Quinn and Dussaillant (2014a) respectively took into account a partition of soil water between "mobile" and "immobile" phases, and a "rapid" flow in macropores which is assumed to be responsible for deeper contaminant migration than predicted by "single-porosity" models (Quinn & Dussaillant, 2014b); Massoudieh and Ginn (2007; 2008) developed a model including colloid transport in infiltration basins, and compared its performances to those of the "classic" model. The physical chemistry of soil was modelled with various sets of equations, either assuming local equilibrium between the solid and aqueous phase (*i.e.* instantaneous sorption), or taking into account a first-order kinetic model. Legret et al. (1999) used real precipitation records and infiltration data from an experimental site, whereas other simulations were run with quite simplistic rain patterns (*e.g.* cyclic alternation of dry weather and rainfall with constant intensity in Dawson et al. (2009)). The contaminant concentration in runoff was systematically assumed constant, even if many studies have demonstrated its high intra- and inter-event variability (Kayhanian, et al., 2012).

This diversity of approaches brings about several questions relative to the level of complexity to be used for modelling both the water fluxes, and the interactions between pollutants and soil. The objective of this paper is to present different modelling options and hypotheses to predict accumulation and transfer of contaminants through an infiltration facility, to compare them in a generic case, and to discuss their interest, focusing on one particular species (Zn).

THEORETICAL BACKGROUND AND GOVERNING EQUATIONS
Modelling the fate and transport of contaminants in the soil of SUDS is a specific application of a reactive transport model in the vadose zone. The general structure of such a model consists of three sets of equations, describing respectively: (*i*) water flow in soil, (*ii*) solute transport in infiltrating water, and (*iii*) metal reactivity with the soil matrix. For each part, several options may be chosen according to the precision requirements and the available data.

Hydrodynamics
The governing equation for water fluxes in unsaturated soils is the Richards equation, which derives from the continuity equation and the Darcy-Buckingham law:

$$\frac{\partial \theta}{\partial t} = \nabla \cdot \left(K(\theta)\, \vec{\nabla}(h - z) \right) = \frac{\partial}{\partial z}\left(K(\theta)\left(\frac{\partial h}{\partial z} - 1 \right) \right) \tag{1}$$

where θ is the soil water content [L^3.L^{-3}], t is the time [T], K is the hydraulic conductivity [L.T^{-1}], dependent on the water content, h is the pressure head [L], and z is the vertical coordinate (increasing downward) [L]. The resolution of this equation requires the knowledge of the soil retention (h–θ) and permeability (K–θ) curves. In the absence of hysteresis, the van Genuchten-Mualem relationships are widely used (Mualem, 1976; van Genuchten, 1980):

$$\theta(h) = \begin{cases} \theta_r + \dfrac{\theta_s - \theta_r}{\left[1 + \left| \dfrac{h}{h_0} \right|^n \right]^m} & h < 0 \\[4mm] \theta_s & h \geq 0 \end{cases} \tag{2a}$$

and

$$K(\theta) = \psi\left(\frac{\theta - \theta_r}{\theta_s - \theta_r} \right) K_s \quad \text{with} \quad \psi(u) = \sqrt{u}\left[1 - \left(1 - u^{1/m} \right)^m \right]^2 \tag{2b}$$

where θ_r and θ_s are the residual and saturated water contents, respectively [L^3.L^{-3}], h_0 is a scale parameter corresponding to a reference pressure head [L], n is a van Genuchten shape parameter [-], $m = 1 - 1/n$, and K_s is the saturated hydraulic conductivity [L.T^{-1}]. All those parameters depend on the nature and characteristics of the soil.

Transport

Solute transport is generally described by the classical advection-dispersion equation, based on Fick's law and a mass balance on the considered chemical species, with an additional term S [M.M^{-1}] accounting for the total pollutant concentration in the solid phase:

$$\frac{\partial}{\partial t}(\theta C + \rho S) = \nabla \cdot \left(-\vec{q}C + \theta D \vec{\nabla} C \right) = -\frac{\partial}{\partial z}(qC) + \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z} \right) \tag{3}$$

where C is the total solute concentration [M.L^{-3}], ρ is the bulk density of the soil [M.L^{-3}], q is the Darcy velocity [L.T^{-1}] and D is the hydrodynamic dispersion coefficient [L^2.T^{-1}], which includes both mechanical dispersion and molecular diffusion, and is calculated as:

$$D = D_m + \alpha_L \frac{q}{\theta} \tag{4}$$

where D_m is the molecular diffusion [L^2.T^{-1}] and α_L is the longitudinal dispersivity [L], which is supposed to be an intrinsic characteristic of the media. Gelhar et al. (1992) conducted a literature review about field-scale measurements of longitudinal dispersivity, and compiled "reliable" values[1] ranging between less than 1 cm and several meters, the median being 79 cm.

The advection-dispersion equation has been shown not to simulate contaminant fluxes accurately in cases the pore size distribution of soil is heterogeneous (Kartha & Srivastava, 2008). So as to take into account a fraction of immobile water in soil, dual-porosity models were first introduced by Coats and Smith (1964), assuming that the total volumetric water content may be written as:

$$\theta = \theta_m + \theta_{im} \tag{5}$$

where the subscripts m and im refer to the mobile and the immobile regions, respectively; therefore θ_m is solution of the Richards equation (1) whereas variations of θ_{im} are only due to rate-limited water exchanges. The convective-dispersive transport is restricted to the mobile region, and the

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[1] The reliability criteria are explained in details in the original paper.

contaminant transfers between both regions are modelled as a Fickian diffusive flux; mass balances lead to the following two equations:

$$\frac{\partial}{\partial t}(\theta_m C_m + f\rho S_m) = -\frac{\partial}{\partial z}(qC_m) + \frac{\partial}{\partial z}\left(\theta_m D \frac{\partial C_m}{\partial z}\right) - \lambda(C_m - C_{im}) \tag{6a}$$

$$\frac{\partial}{\partial t}(\theta_{im} C_{im} + (1-f)\rho S_{im}) = \lambda(C_m - C_{im}) \tag{6b}$$

where f is the fraction of sorption sites in contact with mobile water [-], and λ is a mass transfer coefficient [T^{-1}].

Physical chemistry
Even if the retention of metals onto the soil matrix results from a combination of various sorption mechanisms, it is quite common to give a global, empirical description via a sorption isotherm, *i.e.* a mathematical relationship between the total concentrations in the liquid and solid phases at thermodynamic equilibrium. This approach was proven to describe accurately HM sorption onto soil components (Ho, et al., 2002; Jang, et al., 2005); furthermore, Michel et al. (2007) showed that using a mechanistic model does not improve its efficiency for predicting HM transport in soil columns. The most frequent expressions are the linear, Langmuir and Freundlich equations, to wit:

$$S = K_D C \quad ; \quad S = S_{max} \frac{K_L C}{1 + K_L C} \quad ; \quad S = K_F C^{\beta} \tag{7}$$

where K_D is a partition coefficient [L^3.M^{-1}], S_{max} is the maximum sorption capacity in the Langmuir formalism [M.M^{-1}], K_L is a scale parameter [L^3.M^{-1}], and K_F [L$^{3\beta}$M$^{-\beta}$] and β [-] are two empirical parameters in the Freundlich formalism. It may be postulated that local equilibrium is reached instantaneously, or a rate-limited process may be taken into account; the combination of both approaches leads to the "two-site model", wherein sorption is assumed to be instantaneous for a fraction of the sorbent, and rate-limited for the remainder (Maraqa, et al., 2011):

$$S = S_1 + S_2 \tag{8a}$$

with

$$S_1 = p\varphi(C) \tag{8b}$$

and

$$\frac{\partial S_2}{\partial t} = \omega\big((1-p)\varphi(C) - S_2\big) \tag{8c}$$

where p is the fraction of sites on which sorption is instantaneous [-], φ is the sorption isotherm, and ω is the first-order rate coefficient [T^{-1}]. Uptake by plants is generally neglected in modelling studies, since this phenomenon has been shown to account for a small fraction of the global retention (Sun & Davis, 2007).

MATERIAL AND METHODS
The modelled device is a generic stormwater infiltration basin, with a one-meter-thick homogeneous soil layer. Atmospheric boundary conditions (*i.e.* rainfall and evapotranspiration) are implemented at soil surface. The upper water flux in the absence of ponding is given by:

$$K(\theta)\left(1 - \frac{\partial h}{\partial z}\right)\bigg|_{z=0} = I(t) - E(t) \tag{9a}$$

where I and E are the inflow and evapotranspiration (ET), respectively [L.T^{-1}]. When ponding occurs, the water flow in the upper soil layer becomes head-dominated, and the corresponding boundary condition changes to:

$$\theta|_{z=0} = \theta_s \tag{9b}$$

The effective drainage area (considering the runoff coefficient) is supposed to be N times wider than the cell surface area (N being a model parameter), so that:

$$I(t) = NR(t) \qquad (9c)$$

where R is the rainfall intensity [L.T^{-1}]. We assumed that the basin has no structural outlet, hence the incoming water infiltrates/evaporates completely. In the transport module, a Dirichlet boundary condition was applied for the solute concentration in soil water:

$$C|_{z=0} = C_0(t) \qquad (10)$$

where C_0 is the concentration in the runoff [M.L^{-3}]. When ponding occurred, we postulated a complete mixing between pond and runoff water.

Input data

Soil data were taken from Sastre et al. (2007), in which a thorough characterization of several contrasting soils was carried out, including sorption-desorption tests. The selected soil was a Calcic Luvisol (characterized by a textural contrast between the A and the B horizon) with a silt-loamy texture and a neutral pH; its main physical and physicochemical characteristics are summarised in Tables 1 and 2. The specific soil parameters of the infiltration basin were obtained from its texture and field capacity, via pedotransfer functions developed by Schaap et al. (2001). 15 years of hourly rainfall and daily potential ET recorded in the region of Paris, France, were used as input data for the simulation; hourly sinusoidal variations of potential ET were generated according to sunshine duration data. The mean event concentration in the runoff water was derived from a series of measurements in a residential catchment in the Paris area; a lognormal distribution was fitted to the data, the density function being:

$$f_{C_0}(x) = \frac{1}{x\sigma\sqrt{2\pi}}\exp\left(-\frac{(\ln x - \mu)^2}{2\sigma^2}\right) \qquad (11)$$

where μ and σ are the location and scale parameters of the distribution, respectively, which are given Table 3 along with the statistical moments of the variable C_0.

The governing flow and transport equations presented above were solved numerically using Galerkin-type linear finite element schemes.

Table 1. Main physical and physicochemical properties of the soil chosen for the numerical simulations. [1]FC: Field Capacity.

Sand	Loam	Clay	θ_{FC}[1]	pH	C_{org}	CaCO$_3$	CEC	Fe$_2$O$_3$	CaO
[%]	[%]	[%]	[%]		[%]	[%]	[cmol$_c$.kg^{-1}]	[%]	[%]
9.5	70.3	20.2	30.1	7.0	1.46	0.3	17.5	3.2	1.0

Table 2. Parameters of the Linear, Langmuir and Freundlich isotherms for Zn (Sastre, et al., 2007).

Linear	Langmuir		Freundlich	
K_D	K_L	S_{max}	K_F	β
[l.kg^{-1}]	[l.mg^{-1}]	[mg.kg^{-1}]	[l$^\beta$.mg$^{1-\beta}$.kg^{-1}]	[-]
440	0.45	960	200	0.5

Table 3. Main characteristics of the concentration C_0 in runoff water.

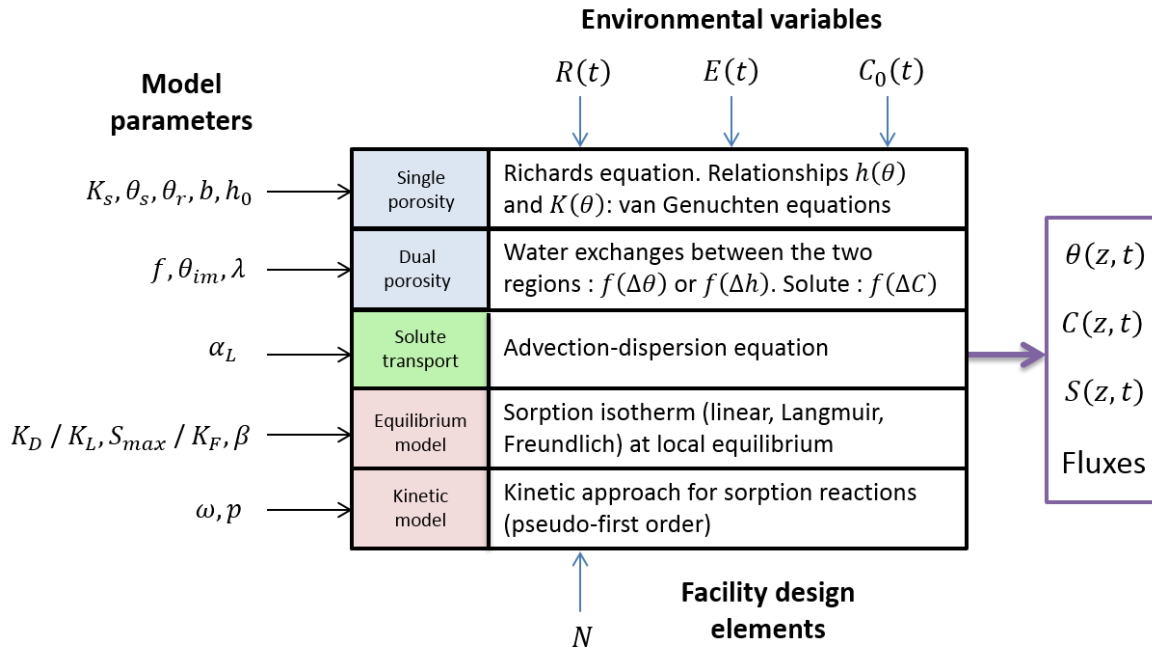| Statistical moments		L.-N. distribution parameters	
Mean	St. dev.	μ	σ
[µg.l^{-1}]	[µg.l^{-1}]		
262	103	5.5	0.49

Figure 1. General structure of the model: modelling options and input parameters to describe (*i*) hydrodynamics, (*ii*) contaminant transport, (*iii*) sorption on solid phase.

RESULTS AND DISCUSSION

Influence of variable C_0

So as to determine the bias introduced by the hypothesis of a constant concentration in runoff water, a series of 1000 simulations was carried out, generating a random value of $C_0(t)$ for each rainfall event. Sorption was supposed to follow a Freundlich isotherm at local equilibrium, and we set the values of N and α_L to 30 and 10 cm, respectively. The coloured envelopes on Fig. 2 represent the interval [Mean $\pm$ St. dev.] of the predicted concentrations in soil at each depth. The solid lines correspond to a constant C_0 over the whole period. The inter-event variability of runoff event mean concentrations causes significant uncertainties about the soil surface concentration (between 0 and 20 cm), but does almost not affect the rest of the contamination profile; it is not likely to modify the global migration dynamics, nor the long-term bottom fluxes of contaminants, so the simplifying assumption may be justified in that context.

Influence of the sorption isotherm

The equation used to fit the sorption isotherm has an influence on the shape of the contamination profile (Fig. 3). The linear and Langmuir models give similar results, since they are almost equivalent at low concentrations, while the use of a Freundlich isotherm may lead to contrasting conclusions. For example, no breakthrough is expected for 15 years with the latter model, whereas

Zn is predicted to reach 1 m depth before 10 years using the linear or Langmuir formalism. This finding has noteworthy experimental implications, since the concentrations ranges used for most sorption tests are not representative of usual concentrations in runoff; therefore the "effective" part of the isotherm is often extrapolated. The behaviour of the contaminants in batch systems needs to be characterized precisely so as to accurately predict their long-term migration in soils.
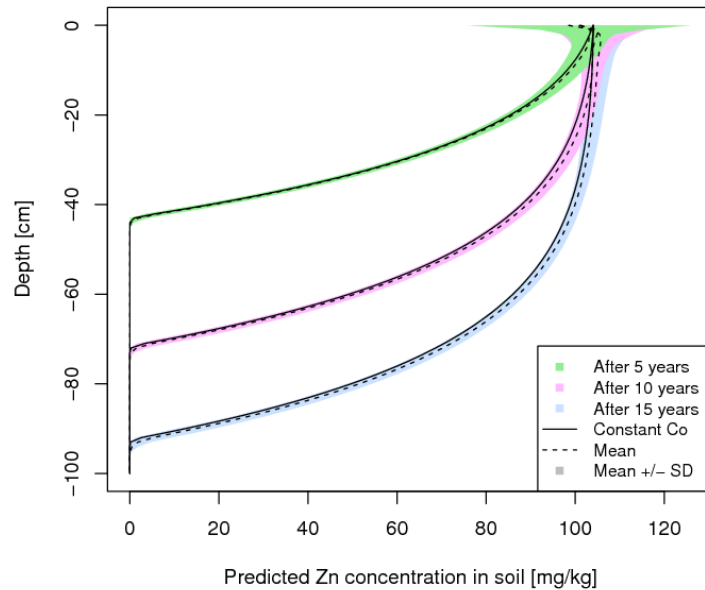

Figure 2. Predicted Zn concentration in soil after 5, 10 and 15 years of operation, using a constant (solid lines) or a random (dashed lines and coloured envelopes) concentration in stormwater.
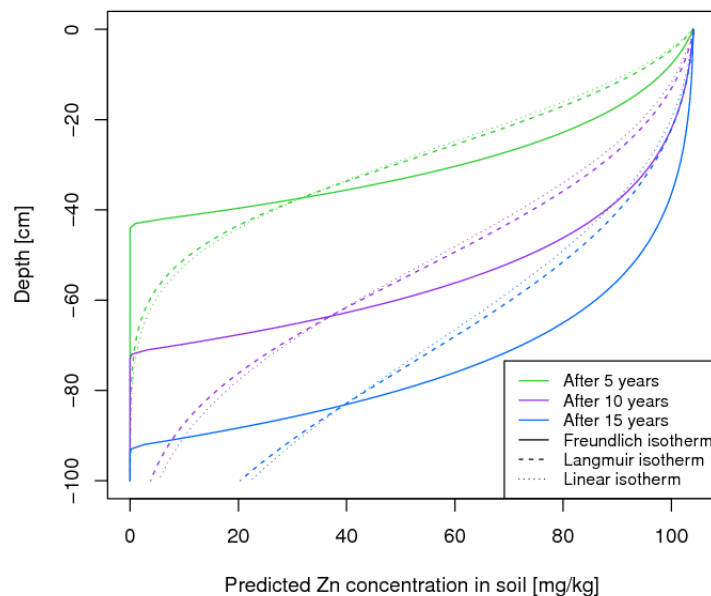

Figure 3. Predicted Zn concentration in soil after 5, 10 and 15 years of operation, using a Freundlich (solid lines), Langmuir (dashed lines) or linear (dotted lines) sorption isotherm fitted with the same experimental data.

Influence of the rate-limited processes

The contamination profiles obtained with the hypothesis of local equilibrium were compared to the results of the kinetic model. Different values may be found in the literature for the rate constant ω, hence a "worst-case scenario" was adopted in this study, considering a slow reaction mechanism with $p = 0$ (*i.e.* no instantaneous sorption sites). In most HM sorption-desorption tests using a batch method, *e.g.* in the OECD Guidelines for the Testing of Chemicals (2000), equilibrium is supposed to be reached within 24 h. For a first-order phenomenon, the typical time constant should therefore be lower than 8-10 h, so we selected $\omega = 0.1$ h^{-1} as a lower limit for the kinetic processes. It may be seen on Fig. 4 that the non-equilibrium model causes very little differences in solute concentrations; the maximum difference between both contamination profiles is lower than $C_0/25$, and tends to decrease with α_L and N. Considering the 15-year-long simulation, and the whole soil layer, the mean flow rate in soil is 0.8, 2.5 and 4.0 mm.h^{-1} for $N = 10$, 30 and 50, respectively, so the residence time of water in a 5-cm-deep soil layer is higher than 12 h; this time may be sufficient to ensure most metal sorption onto the soil matrix. Furthermore, dispersion significantly reduces the impact of kinetic sorption on the contamination profiles (Fig. 4.b), with the contribution of both soil's dispersivity and drainage area, since q, and consequently D, increase with N (equation 4).

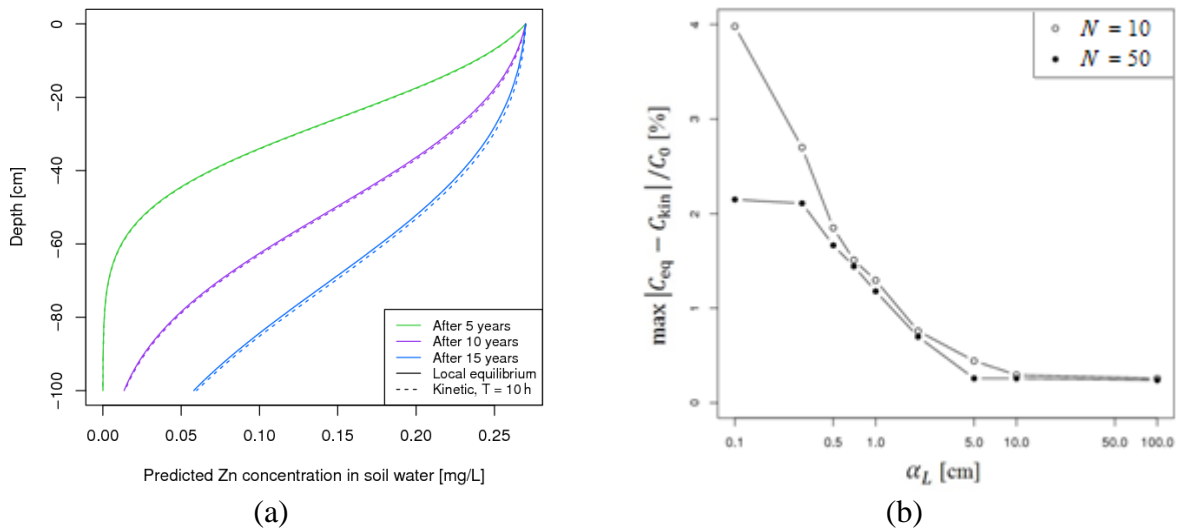(a)   (b)

Figure 4. (a) Comparison of the contamination profiles predicted by the equilibrium and the kinetic models after 5, 10 and 15 years of operation, for $\alpha_L = 10$ cm and $N = 30$; (b) maximum difference between both profiles relative to C_0, as a function of α_L and N.

Influence of structural parameters

Considering a soil with given sorption properties, whatever the complexity of the hydrodynamic and transport models, the two parameters which seem to have most effect on the contamination profiles are the "concentration factor" N, which determines the amount of inflow water in given meteorological conditions, and the soil's dispersivity α_L (or in an almost equivalent manner, the dispersion coefficient D), which significantly modifies the shape of the contamination profiles (Fig. 5). However, in every modelling study mentioned hereinabove, very little attention has been given to the estimation of these two parameters, nor to the sensitivity of the results. The upper boundary condition for water flux was often simplistic, and in some cases the authors implicitly assumed that N equals to unity. The existence of a runoff concentration in SUDS is a major difference with studies focusing on contaminated soils in other contexts (*e.g.* industrial areas), for which the assumption of rainfall being the only inward water flux is reasonable.
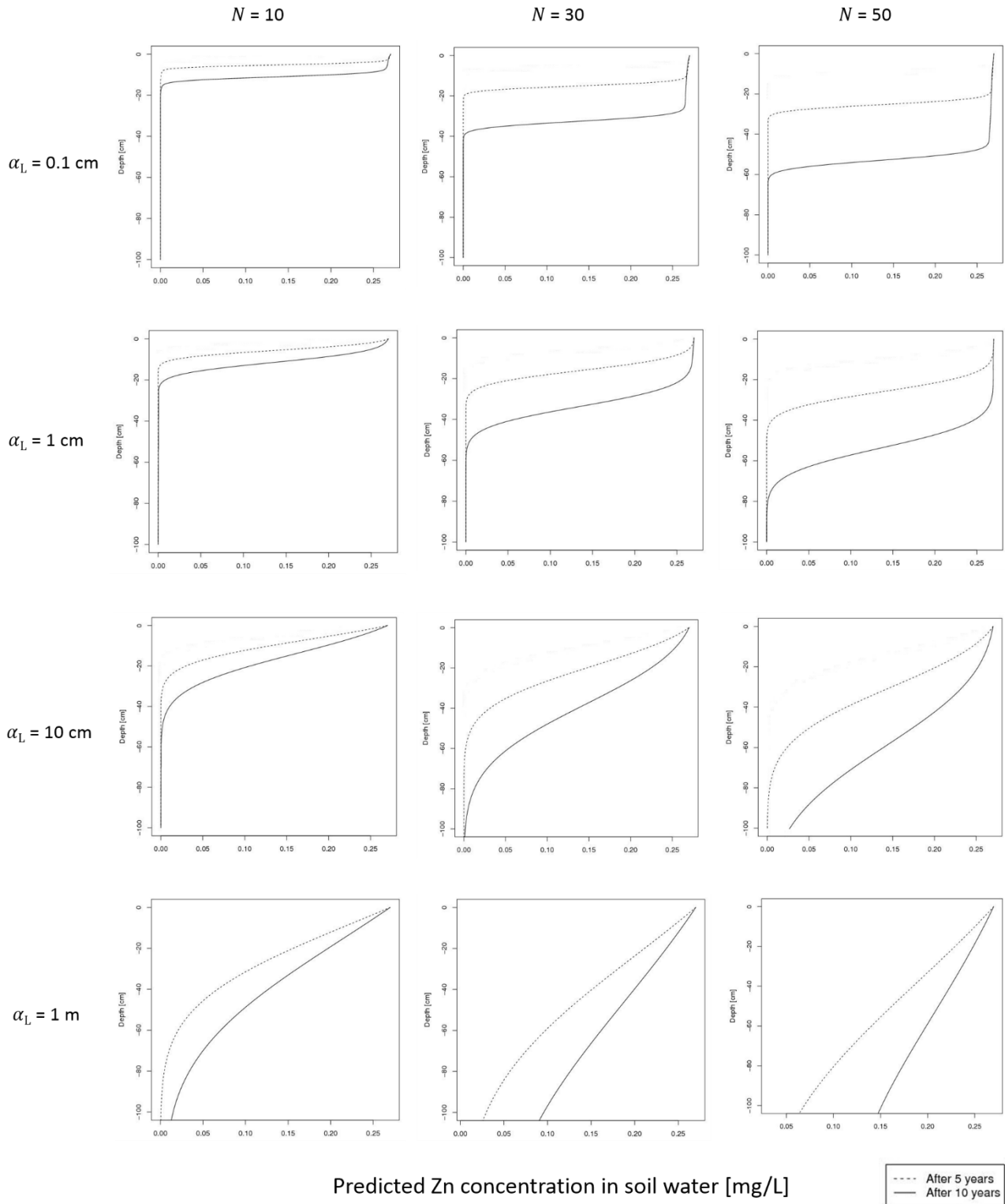
Figure 5. Displacement of the contamination profile with operating time, after 5 (dashed lines) and 10 years (solid lines) respectively, as a function of α_L and N.

As regards the dispersion coefficient, either the chosen value for the simulation was not given, or it was derived from another study, in which the context was generally different. Yet, as mentioned earlier, the wide range of available values in the literature raises questions about the relevance of this approach. Moreover, the laboratory-scale measurements of α_L or D, in soil columns experiments, have been shown to underestimate the *in-situ* values (Batta & Murty, 1982; Lamy, et al., 2008). A correct estimation of the dispersion parameter is likely to improve the prediction of the contaminants transport in SUDS better than other specific modelling options.

Contaminant fluxes and lifespan assessment of the devices
Similar to the concentration profiles, the contaminant fluxes appear to be highly sensitive to the soil's dispersivity for given physicochemical retention properties. A spatiotemporal plot of the cumulative downward fluxes is displayed on Fig. 6, assuming local equilibrium and linear sorption. So as to handle the long-term risks of contaminant transport to groundwater beneath SUDS, it would be convenient to appraise a "lifespan" of these facilities which would minimize downward fluxes. The present modelling study highlights the need for an accurate estimation of the dispersivity, and suggests that "source-control" techniques with low values of the N parameter seem to have a better potential for contaminant retention than centralised infiltration basins.
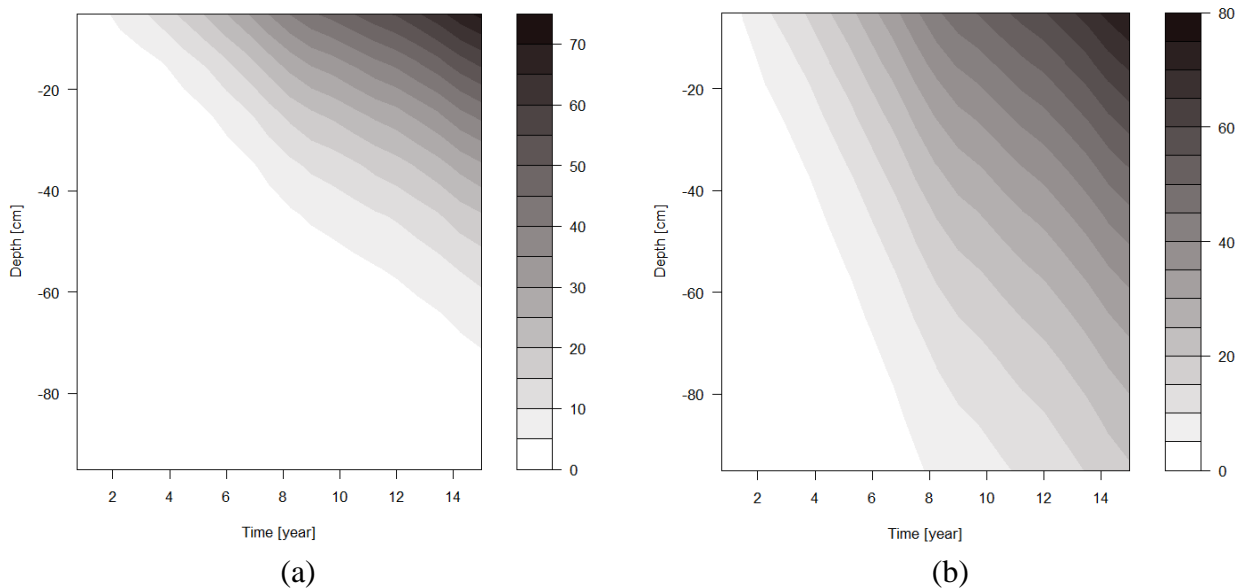

Figure 6. Downward Zn cumulative fluxes [kg.m^{-2}] at depth z over time t, for $N = 30$ and (a) $\alpha_L = 10$ cm, (b) $\alpha_L = 1$ m.

CONCLUDING REMARKS AND PERSPECTIVES
Among the variety of assessed modeling options and simplifying assumptions, the parameter which was found to have most influence on the contaminants spreading in soil was the dispersivity of the media, which pertains to the "basic" transport module and whose determination may be somewhat laborious. Besides, there is no "typical" value of this parameter, since *in-situ* experimental measurements vary within more than two orders of magnitude and laboratory-scale studies tend to underestimate it. The uncertainty in the contamination patterns caused by a biased estimation of the dispersion parameter is likely to be larger than the accuracy gained with a more complex modelling framework.
The "concentration effect" due to a drainage area larger than the infiltration zone also causes significant differences in the migration dynamics. This outcome is likely to be accentuated if non-

homogeneous water infiltration is taken into account, especially for small rainfall events during which stormwater may not spread in the entire device.

All the results shown were derived for a given soil, and did not consider the inter-sites variability of the hydrodynamic and physicochemical properties of the soil. The residence time of water is generally lower in highly permeable media, in which case the conclusions about the rate-limited processes may not hold.

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