**Supplementary information**

**Supplementary information A: Homogenization and derivation of macroscale model with multiple space scale asymptotic expansion**

The macro-scale equations for average solute concentration and the effect of non-uniform patch distribution are derived following the method of homogenization (Pavliotis & Stuart, 2008). We expand the concentration variables asymptotically in powers of as,

|  |  |  |
| --- | --- | --- |
|  |  |  |
| , |  | (SI1) |
| . |  |  |

The concentration variables in Equation (SI1) are periodic with respect to. The key assumption of homogenization is that the micro- and macro-scale variables may be treated independently. Hence, we write and substitute Equations (SI1) into Equations (1 main text), to solve in ascending powers of . Collecting terms at we obtain

|  |  |  |
| --- | --- | --- |
|  |  | (SI1.1) |
|  |  | (SI1.2) |
|  |  | (SI1.3) |
|  |  | (SI1.4) |
| . |  | (SI1.5) |

Equation (SI1.1) and the boundary condition (SI1.2) are satisfied for , i.e setting epsilon to zero, the solute concentration is independent of the microscale geometry. At this order of , the fast reaction has already occurred and the surface concentration at the fast sorption site equals the solution concentration, i.e., . Finally, we assume that the soil sample contained no adsorbed solute prior to the simulation and, therefore, . We note that is not uniquely defined at this order, which is common to homogenization problems. Therefore, we expand to higher orders to close the problem. At we obtain

|  |  |  |
| --- | --- | --- |
| =0 |  | (SI2.1) |
| = 0 |   | (SI2.2) |
|  |  | (SI2.3) |
|   |   | (SI2.4) |
|  |  | (SI2.5) |

Equations (SI2) have a solution given by

|  |  |  |
| --- | --- | --- |
|  , |  | (SI3) |

where is any function of the macroscale variable and satisfies the cell problem as follows:

|  |  |  |
| --- | --- | --- |
|   |  | (SI3.1) |
|  |  | (SI3.2) |
|   |  | (SI3.3) |
|  with period 1 |  |  |

Equation (SI2.4) can be solved to calculate with the solution of previous order concentration terms and Equation (SI3). Solution of Equation (SI2.5) gives and provides the value of .

At this point we note that is still not uniquely defined. In addition, is not uniquely defined. Expanding to we obtain

|  |  |  |
| --- | --- | --- |
|  , |  | (SI4.1) |
| , |  | (SI4.2) |
| , |  | (SI4.3) |
|  |  | (SI4.4) |
| . |  | (SI4.5) |

Equations (SI4) are a set of non-homogeneous elliptical equations for . So that these equations have a solution, we require that the total flux into the domain is zero. Integrating Equation (SI4.1) over , and applying the divergence theorem with Equation (SI4.2)–(SI4.3) we obtain

|  |  |  |
| --- | --- | --- |
| , |  | (SI5) |

where, and . The total area of the binding aggregate surface domain, . is the volume integral over the liquid volume domain. We can also write , where is the Kronecker delta. We calculate **D** by solving the cell equations (SI3.1)–(SI3.3) at the microscale domain. The solution procedure is given in detail in Appendix B.

The solvability condition for Equations (SI4) has been established, we can now solve equations (SI4) and find

|  |  |  |
| --- | --- | --- |
| , |  | (SI6) |

where satisfies equations (SI3), satisfies the cell problem

|  |  |  |
| --- | --- | --- |
| , |  | (SI6.1) |
| , |  | (SI6.2) |
| , |  | (SI6.3) |
|  with period 1 |  |  |

and γ satisfies the cell problem

|  |  |  |
| --- | --- | --- |
| , |  | (SI7.1) |
|  |  | (SI7.2) |
| , |  | (SI7.3) |
|  is periodic with period 1. |  |  |

Finally, to calculate the effect of uneven patch distribution at the macroscale we expand to

|  |  |  |
| --- | --- | --- |
|  |  | (SI8.1) |
|   |  | (SI8.2) |
|  |  | (SI8.3) |
|  |  | (SI8.4) |
|  |  | (SI8.5) |

Again, we require that Equations (SI8) have a solution. By integrating Equation (SI8.1) with the divergence theorem and Equations (SI8.2) - (SI8.3) we obtain

|  |  |
| --- | --- |
|  | (SI9.1) |

Equation (SI9) is coupled with Equation (SI2.4) to calculate as

|  |  |  |
| --- | --- | --- |
|  |  | (SI9.2) |

where

|  |  |  |
| --- | --- | --- |
|  |  | (SI10.1) |
|  |  | (SI10.2) |

The detailed calculation procedure of **E** and **f** is given in Supplementary information B.

**Supplementary information B: Solution of the cell equations**

In this section we describe the solution algorithm used to solve the cell equations at the microscale. The solutions of cell problems provide the effective parameters which are then up-scaled to solve the homogenized macroscale system. The method of homogenization requires the micro-scale domain to be periodic. However, a true periodic geometry in natural soil is, in general, non-existent. A good approximation to a periodic soil domain can be achieved by reflecting or translating the soil microscale domain in all spatial directions. In this research, we imposed periodicity by reflection because it simplifies the calculation and prevents the appearance of discontinuities in the soil structure. We outline the steps involved in subsampling and meshing to illustrate the generation of a periodic domain in Figure SB1. We note, however, that rather than solving the equations on a periodic domain we solve them in the partial domain , which is obtained from CT imaging, and then we infer the solution in the remaining part of the domain through reflection. This procedure requires careful analysis of the cell problems to determine the appropriate boundary conditions that must be applied on the boundaries and for all . After establishing the boundary conditions required to induce soil periodicity we proceed to solve the cell equations to calculate the homogenized model parameters.

*Solution of*

The solution of in the microscale domain is required to calculate the effective diffusion coefficient tensor, . See Equations (7), (9), (11) and (12) in the main text and Equation (SA5) in SI A. From the soil periodicity with the process of reflection, we find that the -th component of is odd in the direction and even in the directions for . Therefore, the resulting equations and boundary conditions are:

|  |  |  |
| --- | --- | --- |
|  |  | (SI11.1) |
|  |  | (SI11.2) |
|  |  | (SI11.3) |
|  |  | (SI11.4) |
|   |  | (SI11.5) |

where is the boundary of the periodic domain located at and , is the union of boundaries at and for .

*Solution of*

We solve Equations (SI6.1) – (SI6.3) to calculate the third rank tensor, which determines the effect of the non-uniform binding site distribution on solute transport. The tensor in Equations (9) and (12) in the main text accounts for the effect of the phase distribution for fast sorption reactions.

An unintended consequence of the reflection is that the distribution of solute-sorbing patches is also symmetric within a representative volume. This restricts the potential patch distributions to those that are evenly distributed within the representative volume, i.e., it forces them to be more homogeneous. To overcome this and allow the maximum possible variation in patchiness, we consider two possible cases. First, the sorption sites are evenly distributed within the representative soil volume. Second, the location of sorption sites is non-symmetrically distributed. By combining these two cases we can formulate a distribution of sorption sites that is not constrained by the reflected geometry. We illustrate this concept in terms of mathematical functions in Figure SB2. The combination of these cases enables us to construct any random or non-uniform patterns of distribution of binding sites in the domain whilst maintaining the reflected periodicity of the soil.

We find independently of the binding site distribution that is even in all directions for and the volume integrals following Equation (SA10.1) in a periodic microscale soil domain cancel the effect of spatial distribution completely. In contrast, for then is odd in the direction for and and even in the direction . The resulting equations and boundary conditions for the odd distribution are

|  |  |  |
| --- | --- | --- |
|  |  | (SI12.1) |
|  |  | (SI12.2) |
|  |  | (SI12.3) |
|   |  | (SI12.4) |
|   |  | (SI12.5) |

*Solution of*

We solve Equations (SA7.1)–(SA7.3) to calculate the vector **f** in Equation (9) of the main text. The vector **f** captures the effect of spatially distributed binding sites on solute movement for slow sorption reactions. As mentioned earlier, if the surface binding sites are symmetrically or evenly distributed on the soil aggregate surface, then **f** is even in all direction and the volume integrals following Equation (SA10.2) on a periodic microscale soil domain cancel the effect of spatial distribution completely. For an odd distribution of surface binding sites **f** is odd in all directions. We write the resulting equations and boundary conditions for odd distribution as:

|  |  |  |
| --- | --- | --- |
|  |  | (SI13.1) |
|  |  | (SI13.2) |
|  |  | (SI13.3) |
|  |  | (SI13.4) |

**Table S1** Parameter values

|  |  |  |
| --- | --- | --- |
| Symbol | Definition  | Value |
| *A*f | Surface area per unit soil volume of fast sorption sites | 71.82 cm2 cm-3 |
| *A*s | Surface area per unit soil volume of slow sorption sites | 71.82 cm2 cm-3 |
| *D*l | Solute diffusion coefficient in free solution | 1 × 10-5 cm2 s-1 |
| *k*af | Rate constant for fast adsorption | 1.78 × 10-5 cm s-1 |
| *k*as | Rate constant for slow adsorption | 6.67 × 10-7 cm s-1 |
| *k*df | Rate constant for fast desorption | 2.25 × 10-4 s-1 |
| *k*ds | Rate constant for slow desorption | 7.05 × 10-8 s-1 |
| *K*f | Equilibrium solid:solution distribution for fast sorption sites | 5 |
| *K*s | Equilibrium solid:solution distribution for slow sorption sites | 680 |
| *l* | Characteristic microscopic length scale | 0.01 cm |
| *L* | Characteristic macroscopic length scale | 1.0 cm |
| *ε* | Scaling ratio = *l*/*L* | 0.01 |
| *δ*af | Dimensionless parameter for fast adsorption  | 1.78 |
| *δ*as | Dimensionless parameter for slow adsorption  | 6.7 |
| *δ*df | Dimensionless parameter for fast desorption  | 0.257 |
| *δ*ds | Dimensionless parameter for slow desorption  | 0.705 |
|  | Tensor for the geometric tortuosity of the solution diffusion path  | 0.035 |
|  | Tensor to represent the effect of random phase distribution for fast sorption reaction | 8.25 × 10-4 |
|  | Vector to represent the effect of random phase distribution for slow sorption reaction | 0.011 |