

MECHANISM OF DELAYED LEACHING OF HEAVY METALS FROM NATURALLY CONTAMINATED SOILS

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Abstract. *Naturally contaminated soils that contain contaminants deep within the particles may show delayed leaching. To incorporate this, a novel approach for predicting the distribution of contaminants, both in the soil particle and surrounding liquid, is achieved using the finite difference method. The approach is named the “intraparticle pore-diffusion model” and is applied to simulate the batch leaching test of heavy metal contaminated soils. Intraparticle diffusion and sorption equilibrium are considered. The desorption phenomena of heavy metal from soil particles are considered as a one-dimensional, polar-symmetric problem in the spherical coordinate system by supposing soil particles to be porous, perfect spheres. The results indicate that soil constituted of larger particles leach more contaminants at a certain time and faster for a certain leaching amount.*

1 INTRODUCTION

Heavy metals leaked from contaminated soil can be taken into the human body through dispersion into the air or leaching into groundwater, posing a risk of harmful effects on human health. In some areas of Japan, soils are naturally contaminated with arsenic and lead, primarily due to metamorphism and seabed sedimentation in the geological past [1]. While artificially contaminated soils hold contaminants at, or near, their surface, naturally contaminated soils are contaminated entirely by heavy metals on their surface and even inside of the particles. This is because the latter takes in contaminants during sedimentation and metamorphism. Therefore, the two may exhibit different leaching behaviors, and it is necessary to take appropriate measures after properly evaluating the leaching risk.

To evaluate leaching risks correctly, the prediction of how much and when contaminated soils leach heavy metals is necessary. Adsorption and desorption are the phenomena that govern the leaching of heavy metals from the soil. The amount of leaching is determined by the adsorption equilibrium, which is the partitioning of the contaminant between the soil and the solution. Several sorption equilibrium equations have been proposed, such as the linear

equation, Freundlich equation, and Langmuir equation. The partitioning coefficient is affected by various factors such as pH, temperature, sorbate specific surface area, the content of Fe/Mn oxides, and the content of clay [2,3,4,5,6,7]. The leaching kinetics have also been investigated in experiments, and numerical models have been proposed, e.g., Pseudo-first order model (PFO, Lagergren model), and Pseudo-second order model (PSO) [8]. These simple models capture the character of sorption kinetics that show a fast sorption rate initially then followed by a slow one but have no clear relationship with the sorption mechanism. Another approach is to focus on diffusion phenomena inside the adsorbent. Weber and Morris (1963) [9] proposed the kinetic model named the intraparticle diffusion model (IPD model), in this model the adsorption is linear against the square root of time. Wu and Gschwend (1986) [10] and Niedermeier and Loehr (2005) [11] adopted another intraparticle diffusion kinetic model summarized by Crank (1979) [12]. This model assumes that the adsorbent particles are spherical, and that radial diffusion occurs inside the particles due to a concentration gradient of contaminants. From the mathematical considerations, the rate of adsorption/desorption should be affected by the square of the particle diameter [9,12]. Assuming that the contaminant concentration of the liquid phase surrounding sorbent particles is always kept at zero, we can obtain an analytical solution of adsorption [12]. Similar to the hydrophobic compounds, for adsorption/desorption of metals by soils, the intraparticle diffusion effect has been implied. Many desorption tests have been carried out where after artificial adsorption of contaminants on adsorbents [13,14,15]. They reported that after the longer adsorption, the lesser and slower desorption occurred. The possibility was implied that contaminants moving deeper into the sorbent particle, which is difficult to access from the particle surface, via micropores.

Leaching from naturally contaminated soil should be evaluated considering intraparticle adsorption-diffusion phenomena heavy metals are distributed inside the particles. However, in batch leaching tests with a small liquid-solid ratio (L/S) or in actual soils, changes in the concentration of contaminants in the bulk phase cannot be ignored, and the adsorbed and leached portions may interact with each other to determine the leaching rate. In addition, the current Japanese standard regulates that the leaching risk of soils should be evaluated by batch leaching tests using samples sieved through a 2mm mesh screen and shaking for 6 hours (Environment Agency Notification No.46: JLT-46) [16]. In practice, however, soils or rocks up to about 100 mm in diameter are reused or disposed of without crushing. It is necessary to consider whether testing with fine grains can determine the risk of leaching from rocks with larger grain sizes. There are several experimental studies about the influence of soil grain size on leaching behavior from naturally contaminated soils [17,18,19], but few analytical studies.

In this paper, we propose “intraparticle pore-diffusion model”, a numerical model for the kinetics of heavy metal leaching behavior from naturally contaminated soils within a closed system. In the proposed model, the naturally contaminated soil is modeled as an aggregate of porous spherical particles with heavy metals uniformly absorbed into the interior. Heavy metal is assumed to diffuse by its concentration gradient and diffusion phenomena in the intragranular pore are solved as a polar-symmetric problem, and the exchange of heavy metal between the solid surface and intragranular void water in adsorption and bulk phase concentration can be considered simultaneously. It is also assumed that adsorption equilibrium is always kept at the solid-liquid interface within the particle. We apply this model to soils that have the same L/S ratio and different particle size distribution to show the effect of intraparticle diffusion.

2 METHODOLOGIES

2.1 Assumption about soils and simulation conditions

We simulate leaching tests of contaminants, such as arsenic or lead, from naturally contaminated soils or rocks within a closed system. In order to regard contaminants transport within a soil particle as a one-dimensional problem, we pose the following three restrictions on the nature of the soil.

- i. The simulated soils are composed of rigid, spherical particles
- ii. Each particle by itself is porous, and its intraparticle pores are filled with water
- iii. Inside each particle, contaminants are transported into pore water by diffusion and adsorbed/desorbed in solid phases.

We simulate the situation that S [g] of dried, heavy metal contaminated soils is well mixed with V_L [L] of uncontaminated water for T [sec]. The soil is composed of M types of soil particles, each type having radius R_m [cm], number N_m ($1 \leq m \leq M$). When we mix dried soil with uncontaminated water, pores within the soil particles are immediately filled with water as well. That means, we can separate the total water volume V_L into intraparticle pore water V_{pore} and water surrounding the soil particles V_{bulk} ,

$$V_L = V_{\text{pore}} + V_{\text{bulk}}. \quad (1)$$

We can determine the pore water volume as

$$V_{\text{pore}} = \frac{S\theta_{\text{in}}}{\rho_{\text{in}}}, \quad (2)$$

with θ_{in} being the porosity of the particle and ρ_{in} [g/cm³] being the density of the particle. ρ_{in} is expressed using true density of soil solid phase ρ_s [g/cm³],

$$\rho_{\text{in}} = (1 - \theta_{\text{in}})\rho_s. \quad (3)$$

Contaminants are present in the particles, both in the pore water as dissolved state and on the surface of the solid phase as an adsorbed state. The adsorption equilibrium is established simultaneously in all soil particles. The adsorption on the solid phase $q_m(t, r)$ [mg/kg] in a particle of radius R_m is given by

$$q_m(t, r) = K_H C_m(t, r), \quad (4)$$

where K_H [L/kg] is the adsorption constant of contaminants with respect to the soil and $C_m(t, r)$ [mg/L] is the concentration of contaminants in pore water within the particle. Both q_m and C_m are dependent on the leaching time t and the distance from the particle center r with $0 \leq r \leq R_m$. For convenience, we herein define the apparent adsorption $q_m^{\text{app}}(t, r)$ as

$$q_m^{\text{app}}(t, r) = \frac{\theta_{\text{in}} C_m(t, r) + \rho_{\text{in}} q_m(t, r)}{\rho_{\text{in}}}. \quad (5)$$

We can determine the initial distribution of contaminants in pore water within each soil particles C_0 [mg/L] as

$$C_0 = \frac{Q_0 \rho_{\text{in}}}{\theta_{\text{in}} + \rho_{\text{in}} K_H}, \quad (6)$$

where Q_0 [mg/kg] is contaminants leaching potential of the dried soil. Likewise, the initial adsorption q_0 is given by

$$q_0 = \frac{K_H Q_0 \rho_{in}}{\theta_{in} + \rho_{in} K_H}. \quad (7)$$

3.2 Governing equation

Leaching progression appears as an increase in bulk phase concentration $C^{\text{bulk}}(t)$ [mg/L]. Assuming a well-stirred closed system, C^{bulk} at a certain time is uniform in the batch. The increase in bulk phase concentration proceeds with a decrease in apparent adsorption (contaminant mass conservation in the total system),

$$\frac{\partial C^{\text{bulk}}(t)}{\partial t} + \frac{1}{V_{\text{bulk}}} \sum_{m=1}^M N_m \rho_{in} \frac{\bar{q}_m^{\text{app}}(t)}{\partial t} \frac{4}{3} \pi R_m^3 = 0, \quad (8)$$

where $\bar{q}_m^{\text{app}}(t)$ is the average of $q_m^{\text{app}}(t, r)$ in a particle of radius R_m . \bar{q}_m^{app} is calculated by the contaminant mass conservation within a particle,

$$\begin{aligned} \frac{\partial \bar{q}_m^{\text{app}}(t)}{\partial t} \frac{4}{3} \pi R_m^3 &= \int_{V_m} \frac{\partial \rho_{in} q_m^{\text{app}}(t, r)}{\partial t} dV \\ &= \int_0^{R_m} 4\pi r^2 \frac{\partial q_m^{\text{app}}(t, r)}{\partial t} dr, \end{aligned} \quad (9)$$

where V_m [cm³] is the volume of a particle of radius R_m . Focusing on the leaching from each particle, we assume that the contaminant leaching behavior is controlled by only intraparticle diffusion and adsorption/desorption. The rate of diffusion is assumed to obey Fick's first law,

$$J_m(t, r) = -D_e \frac{\partial C_m(t, r)}{\partial r}, \quad (10)$$

with $J_m(t, r)$ [mg/sec · cm²] being the flux of contaminants passing through the spherical shell of radius R_m and D_e [cm²/sec] is the effective diffusivity of contaminants at intraparticle pore water, considering the porosity and tortuosity. Assuming the soil particles to be perfectly spherical, we can reduce the contaminant transport within particles to a one-dimensional problem in spherical coordinates (Crank 1979) [12], the contaminant mass conservation at a small range within a particle is given by

$$\begin{aligned} \rho_{in} \frac{\partial q_m^{\text{app}}(t, r)}{\partial t} &= -\left(\frac{\partial J_m(t, r)}{\partial r} + \frac{2}{r} J_m(t, r) \right) \\ &= D_e \left(\frac{\partial^2 C_m(t, r)}{\partial r^2} + \frac{2}{r} \frac{\partial C_m(t, r)}{\partial r} \right). \end{aligned} \quad (11)$$

Transforming q_m^{app} into the expression written in C_m , equation (11) can be reformulated as

$$\frac{\partial C_m(t, r)}{\partial t} = D_e \alpha \left(\frac{\partial^2 C_m(t, r)}{\partial r^2} + \frac{2}{r} \frac{\partial C_m(t, r)}{\partial r} \right), \quad (12)$$

where

$$\alpha = \frac{1}{\theta_{\text{in}} + \rho_{\text{in}} K_{\text{H}}}. \quad (13)$$

Initially, the distribution of the contaminants within particles is in an adsorption equilibrium while the particles are surrounded by non-contaminated water, i.e., for $0 \leq r \leq R_m$,

$$C_m(0, r) = C_0, \quad q_m(0, r) = q_0, \quad C^{\text{bulk}}(0) = 0. \quad (14)$$

Further, the gradient of C_m in the radial direction is always zero at the center of the particle,

$$\left. \frac{\partial C_m(t, r)}{\partial r} \right|_{r=0} = 0. \quad (15)$$

Lastly, at the surface of the particle C_m is equal to C^{bulk} ,

$$C_m(t, R_m) = C^{\text{bulk}}(t). \quad (16)$$

We named this new model ‘‘intraparticle pore-diffusion model’’ and show an overview of this in Figure 1. To simulate the batch leaching test, we solved equation (12) with the finite difference method.

2 RESULTS AND DISCUSSIONS

Firstly, we simulate a heavy metal leaching test from a soil constituted of particles 2 mm in diameter. Testing conditions are shown in Table 1. By checking the changes in contaminants’ distribution over time both inside a particle and in the bulk phase, we verify the operation of the new model. As the concentration of bulk phase C^{bulk} increases, averaged apparent adsorption \bar{q}^{app} decreases so that the entire mass of contaminant is conserved in the batch system (Figure 2). We also focus on the changes in contaminant distribution inside a particle at regular intervals (Figure 3). It is apparent that overall concentration decreases with time and the gradient of concentration from inside to outside is always kept. With the new model, we can simulate the leaching behavior from each soil particle, where contaminants are released to the bulk phase at the particle surface and then supplied from inside to outside.

Next, we compare the changes in contaminant bulk phase concentration with respect to the sizes of particles. The total mass of the soil remains constant across all test cases; however, particle sizes and particle numbers change, see Table 2 reference. Figure 4 (top) shows the time evolution of the average \bar{q}_m^{app} for all test cases. We note that contaminant leaching takes longer for soils consisting of larger particles than for soils consisting of finer particles. This is because the contaminants need to cross larger volumes by pore diffusion for larger particles than for smaller particles. We define the leaching ratio as

$$\text{leaching ratio [\%]} = \frac{\bar{q}^{\text{app}}}{q_{\text{eq}}} \times 100 = \frac{C^{\text{bulk}}}{C_{\text{eq}}} \times 100. \quad (17)$$

C_{eq} and q_{eq} are the $C^{\text{bulk}}(t)$ and $\bar{q}_m^{\text{app}}(t)$ at ultimate adsorption equilibrium state, respectively. Both C_{eq} and q_{eq} satisfy mass conservation and adsorption equilibrium,

$$Q_0 S = C_{\text{eq}} V_{\text{bulk}} + q_{\text{eq}} S, \quad (18)$$

$$q_{\text{eq}} = K_{\text{H}} C_{\text{eq}}. \quad (19)$$

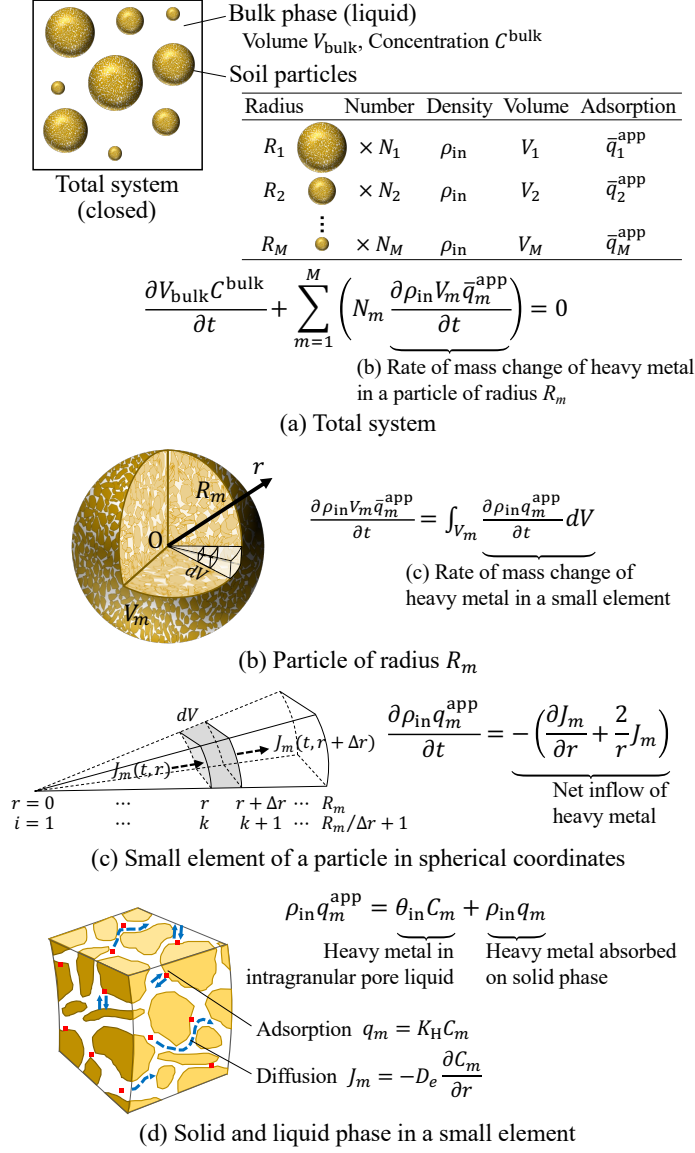

Figure 1: Mass conservation of heavy metal at multiscale

Table 1: Variables for batch leaching behavior analysis

Symbol	Parameter	Value	Unit
V_L	Volume of water	1.00	L
S	Mass of dried soil	0.10	kg
Q_0	Contaminants leaching potential	45.0	mg/kg
θ_{in}	Void ratio in soil particle	0.30	-
ρ_s	True density of soil	2.70	g/cm ³
D_e	Effective diffusive coefficient	1.0×10^{-6}	cm ² /s
K_H	Linear adsorption coefficient	1.96	L/kg

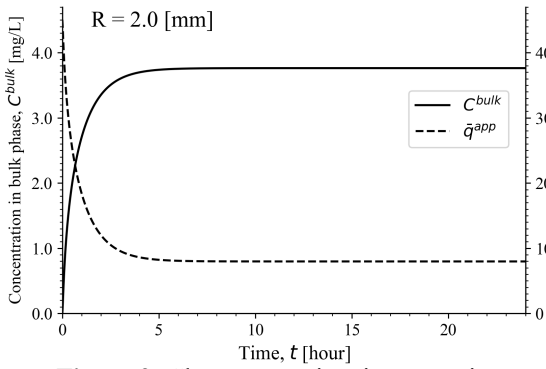


Figure 2: Change over time in contaminant concentration in the bulk phase C^{bulk} and in apparent adsorption \bar{q}^{app}

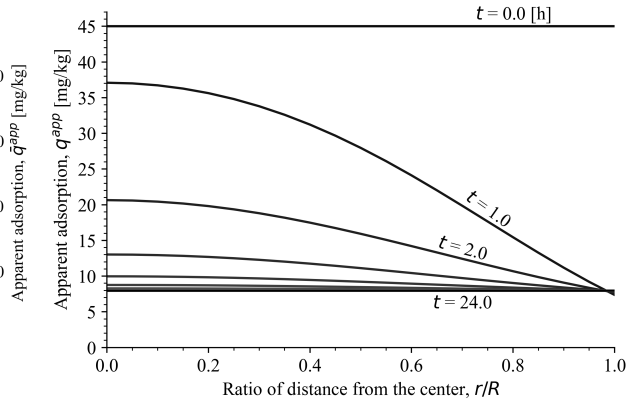


Figure 3: Time-Evolution of the contaminant distribution as a function of relative distance from particle center

Table 2: Variation in testing condition for leaching analysis from soils varying in particle size

Case	Radius R [cm]	Number of particles
1	0.05	101050.75
2	0.10	12631.34
3	0.20	1578.91
4	0.30	467.82
5	0.40	197.36
6	0.50	101.05

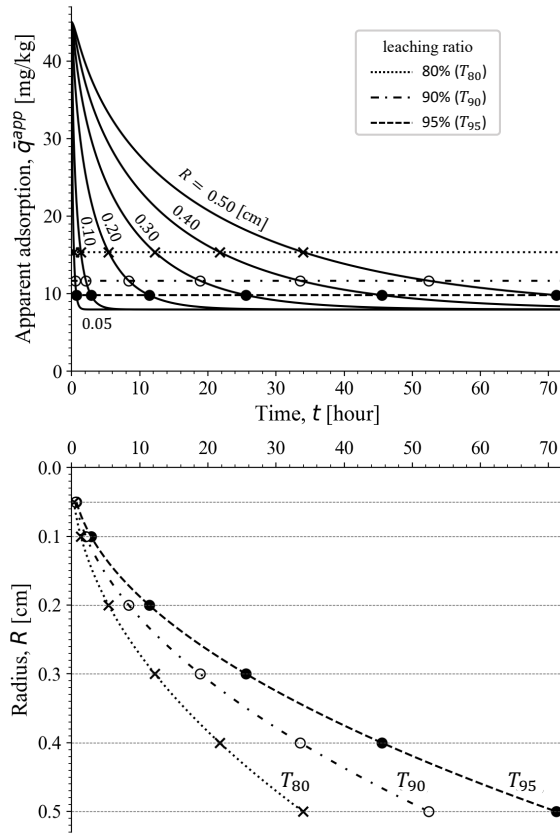


Figure 4: Average adsorption in the solid phase over time (top) and leaching ratio (bottom) over time show particle size effect on leaching kinetics from soils consisting of single sizes particles

The relationship between particle size in each of 6 cases and the time to reach a certain leaching ratio is shown in Figure 4 (bottom). T_i marks the time it takes to reach i [%] of leaching. We

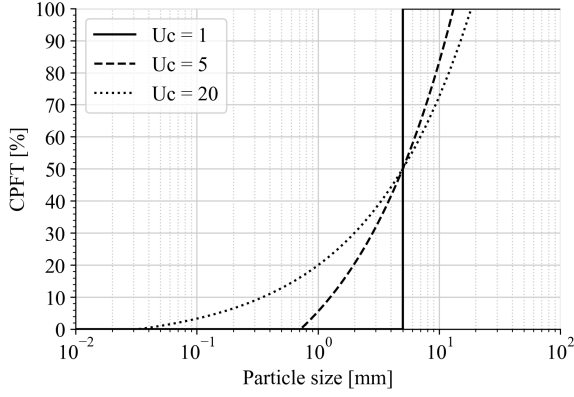


Figure 5: Particle size distribution curves for three different blends

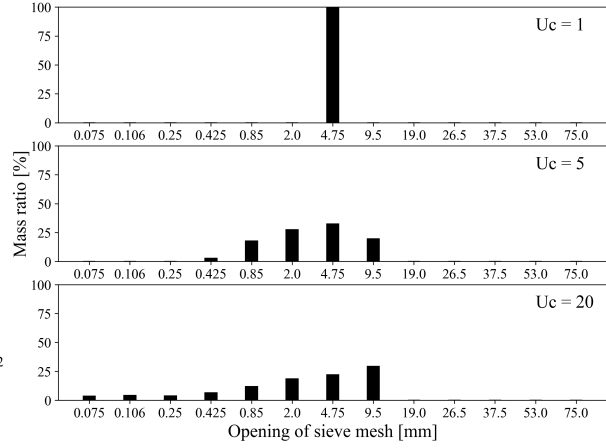


Figure 6: Soil mass ratio on each mesh after sieving three different blends

can show the results in the analysis that the time to reach a certain leaching ratio is relative to the squared radius of soil particles. It was derived by the normalized dimensionless governing equation, see also Crank (1979) [12].

Lastly, we investigate the leaching behavior for soils with particle size distributions. To give a regular particle size distribution, we use the Dinger-Funk equation [20],

$$\text{CPFT} [\%] = \frac{D^n - D_{\min}^n}{D_{\max}^n - D_{\min}^n}, \quad (20)$$

where CPFT (cumulative percent finer than) is the mass ratio of soil particles finer than a particle with diameter D and D_{\max}/D_{\min} is the maximum/minimum particle size. n is the index of the Dinger-Funk equation and we always apply 0.5 to n in the following simulations. To vary particle size distribution curves, we introduce the uniformity coefficient (U_c), defined as

$$U_c = \frac{D_{60}}{D_{10}}. \quad (21)$$

We set three blends of soil specimens with equal D_{50} but different particle size distribution curves, shown in Figure 5. Assuming that these 3 blends are sifted through 13 screens (with opening of sieve mesh 0.075, 0.106, 0.25, 0.425, 0.85, 2.0, 4.75, 9.5, 19.0, 26.5, 37.5, 53.0, 75.0 [mm]), we regard soils on x [mm] sieve are constituted of particles with x [mm] diameter. According to Figure 4, we expect that particles finer than 0.075 [mm] leach contaminants immediately when we consider leaching time on the scale of an hour, so we count soils consisting of finer particles than 0.075 [mm] as soils consisting of 0.075 [mm] particles. Mass ratios of each size of soil particle are compared between 3 blends in Figure 6. We simulate leaching behavior from 3 blends and changes in bulk phase concentration over time are shown in Figure 7. Soils with a wider particle size distribution show a faster leaching behavior in the initial, then slower one at the end than soils with a narrower particle size distribution. It can be considered that the finer particles and the larger particles govern the initial fast leaching and the following delayed leaching, respectively.

As in the cases of equal D_{50} cases, we also considered the cases of equal maximum particle

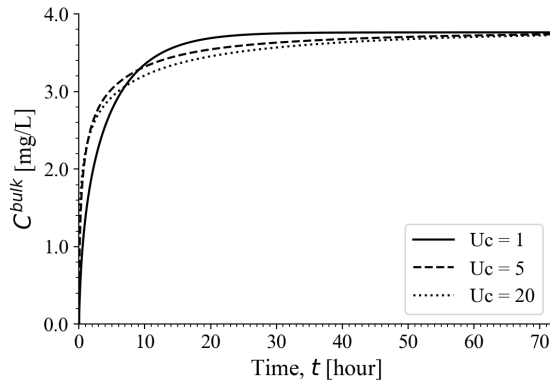


Figure 7: Change over time in contaminant concentration in the bulk phase C^{bulk} for three different blends

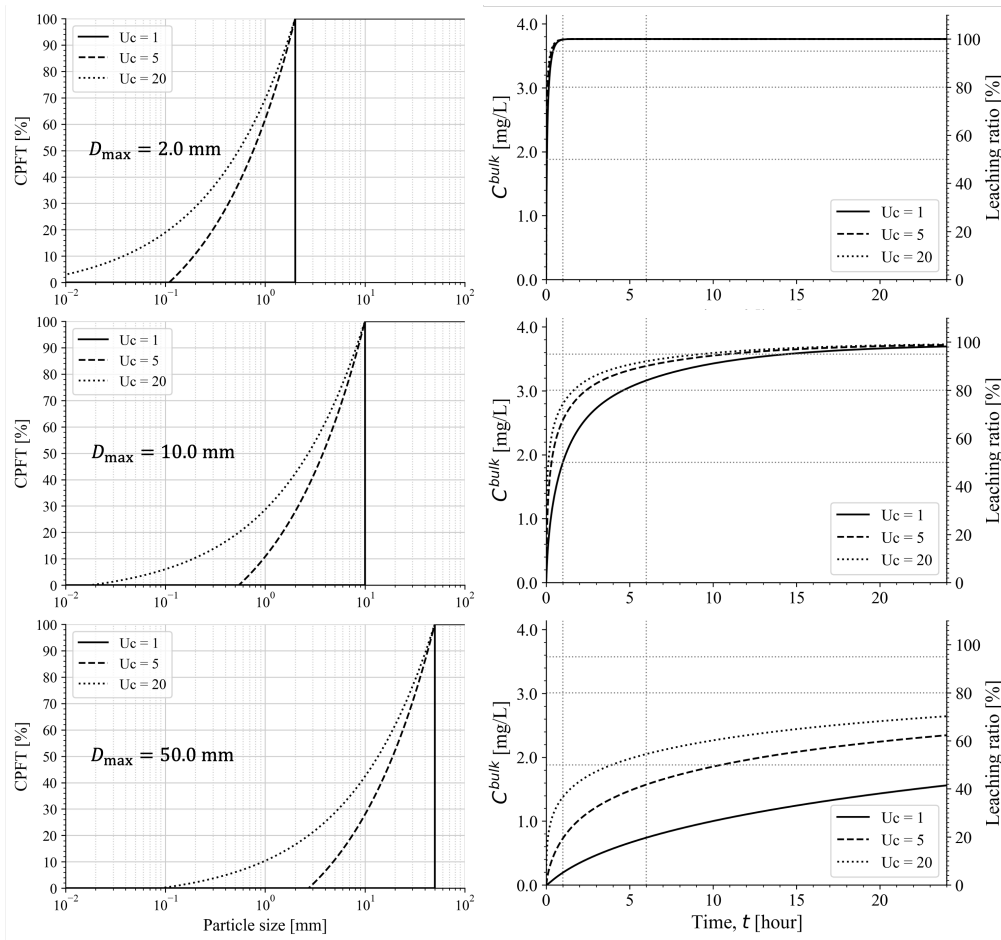


Figure 8: Particle size distribution curves for blends with the same D_{max} and different U_c ($D_{\text{max}} = 2.0, 10.0, 50.0$ [mm], $U_c = 1, 5, 20$) and change of C^{bulk} over time for corresponding blends

size. The particle size distribution curves and leaching analysis results for nine different blends are shown as examples in Figure 8. We analyzed leaching ratios at certain times, varying maximum particle size and U_c , the results are shown in contour maps, Figure 9 (left). From the initial stage, it is obvious that soils with smaller maximum particle sizes present a higher

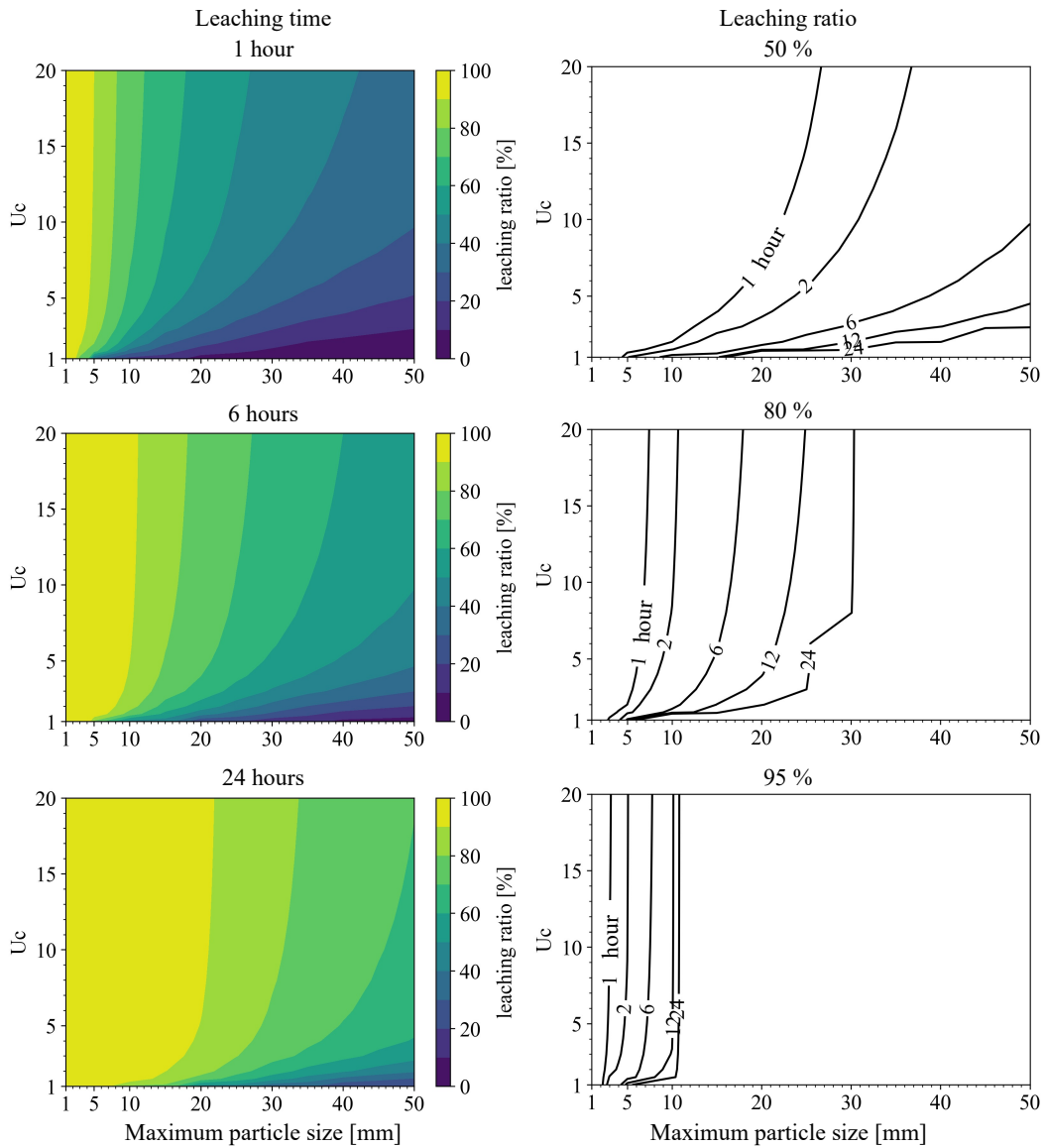


Figure 9: The leaching ratio corresponding to D_{\max} and U_C at a given time (left) and the leaching time corresponding to D_{\max} and U_C required to reach a certain leaching ratio (right)

leaching ratio. As leaching proceeds, we find a relatively low leaching ratio at a low U_C area ($U_C \leq 5$) even at a small maximum particle size area. In addition, we arranged the relationship between leaching time to get a certain leaching ratio and soils with various maximum particle sizes and U_C , see Figure 9 (right). To a certain extent of leaching ratio like 50%, soils with high U_C , containing many fine particles, get earlier to the reaching ratio. To reach a high reaching ratio, however, maximum particle size is the main factor to decide the reaching time. It seems to be difficult to let one index such as the average and maximum particle size of the soil predict the effect of particle size distribution on whole leaching behavior. Since real grounds usually contain various sizes of grains or rocks, an effective way to represent particle size distribution

to reflect its effect on leaching behavior is needed. When it comes to the Japanese standard leaching test method (sieved through 2mm mesh screen, 6 hours shaking), more than 90% of reaching is expected with variables in this study. In case you want to carry out a batch leaching test for soils with ≥ 2 mm particles, having a discussion like Figure 9 and deciding on leaching time is desirable. For example, assume that the JLT-46 leaching test [16] is applied to soils with $D_{\max} = 10$ mm under the condition of Table 2. For a leaching time of 6 hours, we can expect more than 90% leaching for soils with $U_C > 5$, but at most 60% for soils with $U_C = 1$ (see Figure 9, center left). When we extend the leaching time to 24 hours, more than 80% leaching is expected for soils with any U_C (see figure 9, lower left). In this way, after establishing the required leaching ratio, we should determine the leaching time by applying the test conditions such as particle size distribution.

Because we simplified soil structure and leaching processes in our model, some issues arise. Firstly, we assume that all contaminants within the soil particles are accessible to the bulk phase and that soils with some dry mass have the same leaching capacity regardless of particle sizes. For realistic soil particles or rocks, inaccessible intraparticle pores with no or too narrow paths to the bulk phase need to be taken into consideration. Secondly, we do not consider other factors that delay leaching behavior, such as surface diffusion and non-equilibrium adsorption within soil particles. To better predict delayed leaching, it is necessary to improve the adsorption term in the governing equation ($\partial q/\partial t$) so that all delaying factors are considered in the simulation.

5 CONCLUSIONS

We developed a novel numerical method to simulate batch leaching tests of naturally contaminated soils, considering both intra-particle solid adsorption and intra-particle pore diffusion of heavy metals. The leaching behavior was simulated satisfying the contaminant's mass conservation both within the soil particles and total system using a finite difference method. Our model can simultaneously consider the changes in contaminant distribution within soil particles over time and in the surrounding liquid. To solve the phenomena as a one-dimensional problem in a spherical coordinate system, we simplified the individual soil particles as porous spheres of different particle sizes. We found that intraparticle diffusion leads to slower leaching the larger the soil particles are. Our results also suggested that particle size distribution of the soil controls the leaching behavior, as it will affect the rate and degree of leaching. Our method can be a powerful tool, particularly when simulating the batch tests with a low liquid to solid ratio as the changes in the contaminant concentration in the bulk phase cannot be ignored.

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