

Retardation Effect and Mobility of a Heavy Metal in a Sandy Soil

사질토양에서의 중금속의 지연효과와 이동성

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Abstract : Retardation effect of heavy metals in soils caused by adsorption onto the surfaces of solids particles is well known phenomenon. In this study, we investigated the retardation effect on the mobility of a Zn in a sandy soil by conducting batch and column tests. The column test consisted of monitoring the concentrations of effluent versus time known as a breakthrough curve (BTC). We used NaCl and ZnCl₂ solutions with the concentration of 10 g/L as a tracer, and injected them respectively into the inlet boundary of the soil sample as a square pulse type, and monitored the effluent concentrations at the exit boundary under a steady state condition using an EC-meter and ICP-AES. The batch test was conducted based on the standard procedure of equilibrating fine fractions collected from the soil with various initial ZnCl₂ concentrations, and analysis of Zn ions in the equilibrated solutions using ICP-AES. The results of column test showed that i) the peak concentration of ZnCl₂ analyzed by ICP was far less than that of either NaCl or bulk electrical conductivity and ii) travel times of peak concentrations for two tracers were more less identical. The relatively low concentration of Zn can be explained by ion exchange between Zn and other cations, and possible precipitation of Zn in the form of Zn(OH)₂ due to high pH range (7.0~7.9) of the effluent. The identical result of travel times of peak concentrations indicates that the retardation effect is not present in the soil. The only way to describe the prominent decrease of Zn ion was to introduce decay or sink coefficient in the CDE model to account for irreversible decrease of Zn ions in the aqueous phase.

요 약 : 토립자 표면에서의 흡착에 의한 토양에서의 중금속의 지연효과는 잘 알려진 현상이다. 본 연구에서는 배치시험과 주상시험을 수행함으로써 사질 토양에서 Zn의 이동성에 대한 지연효과를 조사하였다. 주상시험은 파과곡선(BTC)으로 알려진 시간에 따른 용액의 농도를 측정함으로써 수행되었다. 추적자로는 10 g/L 농도의 NaCl과 ZnCl₂를 사용하였고, 각각의 용액을 토양시료의 상부경계에 순간주입한 후 정상류 상태에서 배출구로 빠져나온 용탈수의 농도를 EC-meter와 ICP-AES를 이용하여 측정하였다. 배치시험은 표준절차에 근거하여 이루어졌으며, 토양시료로부터 선별된 미세입자들을 다양한 초기농도의 ZnCl₂ 용액과 반응시켜 평형상태의 Zn 이온의 농도를 ICP를 이용하여 분석하였다. 주상시험의 결과는 i) ICP-AES에 의해 분석된 ZnCl₂의 첨두농도는 NaCl이나 충전기전도도로부터 구한 값보다 상당히 낮았고, ii) 두 종류의 추적자 모두 첨두농도의 도달시간은 상당히 일치하였다. 상대적으로 낮은 Zn의 농도는 Zn과 다른 양이온들간의 이온교환반응이 일어났고, 용탈수의 pH가 높은 값의 범위(7.0~7.9)에 있는 것으로 보아 Zn(OH)₂의 형태로 침전되었을 가능성이 있다는 것으로 설명될 수 있다. 첨두농도의 도달시간이 일치한다는 결과는 토양시료에서 지연효과가 일어나지 않았다는 것을 지시한다. Zn 이온의 뚜렷한 감소를 설명할 수 있는 유일한 방법은 CDE 모델에 용액상태에서 Zn 이온의 절대적 감소를 고려하는 감쇄계수(decay or sink coefficient)를 적용하는 것이었다.

Introduction

Recently there has been increasing concerns on the contamination of soil and groundwater by toxic heavy metal elements released from municipal landfills, sewage sludge, mining and industrial wastes. It is therefore essential to un-

derstand the principal processes involved in the fate and mobility of those heavy metal elements in order to prevent possible contamination and establish appropriate remediation measures through risk assessment.

Processes involved in the interaction mechanisms between contaminant, especially heavy metals, and soil are sorption, complexation and precipitation. Sorption, subdivided into three different groups, namely, physical adsorption, specific adsorption, and chemical adsorption, indicates the process in

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which the solutes are partitioned between the liquid phase and the soil particle interface. Of the various phenomena that can contribute to sorption, chemical interaction constitutes the major subject of interest in contaminant-soil interactions. Complexation occurs when a metallic cation reacts with an anion that functions as an inorganic ligand. Precipitation is the converse of dissolution, and in the case of contaminants in the aqueous phase, we consider precipitation to occur when the transfer of solutes from the aqueous phase to the interface results in accumulation of a new substance.

Ion exchange is a specific category of the physical adsorption that is referred to as adsorbent-motivated sorption (Knox *et al.*, 1993); that is, the accumulation occurs due to an affinity of the solid surface for the chemical. Among soil particles, the clay fraction is the most contributing mineral for adsorption. Adsorption of divalent cations originating from heavy metal ions onto fine fractions is well known and brings about retardation effect which slows down the mobility of chemicals in a porous medium. Amount of adsorption from liquid phase to solid surface is commonly given by partitioning coefficient or distribution coefficient that defines the ratio between amount of adsorbed and changes in solute concentration equilibrated between a specific cation and dry soil mass.

Roy *et al.* (1987) studied lead adsorption by Cecil clay loam at pH 4.5 and they found the distribution coefficient to be 232 mL/g. Valocchi (1980) and Valocchi *et al.* (1981) evaluated the transport of ion exchanging solutes during groundwater recharge. Valocchi (1984) also discussed the use of an "effective" partitioning coefficient approach for describing the transport of ion-exchanging contaminants. Ceazan *et al.* (1989) conducted field studies with respect to the exchange and transport of ammonium and potassium in the sand and gravel aquifer and they found that adsorption (exchange) was responsible for the retardation of ammonium (Knox *et al.*, 1993). Perillo *et al.* (1998) recently studied the retardation of FD&C blue no. 1 food dye in leaching experiments and reported that due to adsorption characteristic the dye retarded relative to the wetting front.

Compositional details of soil solids are also contributing factors in establishing the exact processes occurring in the interactions between solutes, the aqueous phase and soil solids. Among various soil solids, clays and humic substances offer the most attractive forces toward toxic chemicals on their surfaces whereas coarse grains such as sands and gravels are recognized to be negligible in the adsorptive capacities. Although these soils have such little capacities, we should not overlook the importance of these soils as an environmental medium for filtering of toxic organic and inorganic chemicals in the subsurface. For instance, artificial wetlands mainly consisting of sandy soils were used for removal of nitrates

with a great success. Bank filtration method (Kong *et al.*, 1998) to render filtering of contaminated groundwater in shallow unconfined sandy aquifer formed by alluvial deposit nearby rivers is upcoming as a promising tool to enhance the quality of groundwater. Another importance can be found by the fact that toxic chemicals such as heavy metals dissolved in river water can flux into the nearby shallow aquifer through the sediments mainly consisting of sandy soils accumulated in the river bed and alluvial deposit.

The objective of this study is thus to investigate the retardation effect of Zn on its mobility in a sandy soil by conducting batch and column tests. The batch test was conducted to obtain the distribution coefficient and retardation factor of Zn under a given pH condition, and the column test to obtain the transport parameters of conservative solute such as NaCl from the relationship between effluent concentration and time known as breakthrough curve (BTC) monitored by an EC-meter, and we finally compared the predicted BTC of Zn with that analyzed by ICP.

Transport Theory

Transport of reactive chemicals showing retardation and decay or degradation in an one dimensional soil system can be described by the following equation (Parker and van Genuchten, 1984):

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - \mu C \quad (1a)$$

$$R = 1 + \frac{\rho_b}{\theta} K_d \quad (1b)$$

where C is the concentration of the solute in the aqueous phase, R is retardation factor, D is dispersion coefficient, V is pore water velocity, μ is decay constant, t is time, x is distance, ρ_b is bulk density, θ is porosity and K_d is distribution coefficient.

The analytical solution of Eq. (1a) for flux concentration in case of pulse type injection of tracer was given by van Genuchten and Alves (1982) using appropriate initial and boundary conditions for finite length of a porous medium:

Initial and boundary conditions:

$$C(x, 0) = C_i \quad (2a)$$

$$\frac{\partial C}{\partial x}(\infty, t) = \text{finite} \quad (2b)$$

$$C(0, t) = \begin{cases} C_0 & 0 < t < t_0 \\ 0 & t > t_0 \end{cases} \quad (2c)$$

solution:

$$i) C(x, t) = C_0 \cdot B(x, t) \quad (0 < t < t_0) \quad (3a)$$

$$B(x, t) = \frac{1}{2} \text{EXP} \left[\frac{(V-u)x}{2D} \right] \text{Erfc} \left[\frac{Rx-ut}{2(DRt)^{1/2}} \right] + \frac{1}{2} \text{EXP} \left[\frac{(V+u)x}{2D} \right] \text{Erfc} \left[\frac{Rx+ut}{2(DRt)^{1/2}} \right]$$

$$u = V \left(1 + \frac{4\mu D}{V^2} \right)^{1/2}$$

ii) $C(x, t) = C_0 B(x, t) - C_0 B(x, t-t_0) \quad (t > t_0)$ (3b)

where C_0 is the concentration of the injected fluid and t_0 is pulse duration.

Materials and Methods

Batch test

The soil type used in this study was a sandy soil, and the particle size analysis is given in Figure 1. The amount of fine fractions less than 23 μm of the sandy soil was 1.45%. These fractions were used for batch test to obtain the distribution coefficient, K_d . The initial concentrations, C_i , of ZnCl_2 used as a tracer in the batch test was 10, 100, 1000, 5000 (mg/L). We allowed shaking of 50 mL solution containing 5 g of dry soil mass for equilibration about 48 hrs. The Zn ion in the equilibrated solution were analyzed using ICP-AES. The pH of the equilibrium solution ranged from 6.95 for the highest initial concentration to 8.15 for the lowest.

Column test

Parallel to the batch test, we conducted also a column test for the soil uniformly packed into PVC cylinder with both diameter and height of 20 cm to investigate the retardation effect of Zn by using two different tracers, NaCl and ZnCl_2 .

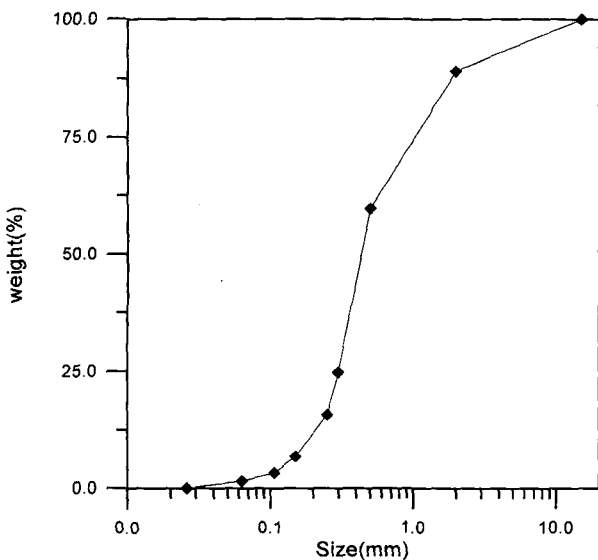


Figure 1. Particle size distribution of the sandy soil.

For the NaCl and ZnCl_2 tracers, we applied a volume of 314 mL solution corresponding to a 1 cm ponding depth above the soil surface with the concentration of 10 g/L as a pulse type before which a steady state condition had been achieved by continuous leaching with tap water having a relatively low electrical conductivity (240 and 212 $\mu\text{S}/\text{cm}$ respectively). The steady state condition was confirmed by both the moisture content and effluent flux density. The moisture content of sandy soil column was monitored by time domain reflectometry (TDR) technique in which a parallel probe was positioned in the middle of soil column, and the travel time of an electromagnetic waveform along the transmission line was retrieved. Under the steady state condition, a constant head of 3 cm was maintained resulting in a Darcian flux equal to 540.7 cm/day. When the infiltration of the injected tracer was completed, the steady state condition with tap water was again imposed on the inlet boundary. A time-series measurement of electrical conductivity was subsequently performed for the effluent exiting from the outlet boundary using an EC-meter. The procedure of column test using the ZnCl_2 tracer was identical with that described above except that the effluent concentration was measured in both the bulk electrical conductivity (mS/cm) and pure Zn concentration (mg/L) using the EC-meter and ICP respectively. In addition, three replicates of the effluents showing the concentration in EC around the peak were collected and analyzed for other cations that were possibly present in the effluents by ion exchange processes.

Calibration of EC measurement

A calibration procedure was required for the EC measurements since they were in the unit of mS/cm. This was conducted by a separate experiment consisting of measurements of ECs for a number of different NaCl and ZnCl_2 solutions with known concentrations in g/L. The solutions were prepared in such a way that a known mass of the tracer was added to the 500 mL of tap water and the mass was gradually increased in a stepwise manner. The result of calibration for the two tracers is shown in Figure 2. It can be seen that the slope of the calibration equation was much steeper for ZnCl_2 solution than NaCl solution indicating that for the same EC the effluent concentration of ZnCl_2 can be higher than that of NaCl.

Data analysis

To obtain the K_d from the batch test, we used a linear adsorption isotherm for two parts of the observed data, expressed as the amount of adsorbed ($\mu\text{g}/\text{g}$) to the equilibrated concentration, C_{eq} (mg/L), since they showed an asymptotic shape having a sharp increase in the lower range of C_{eq} and a moderate increase in the higher range. Then we used the K_d

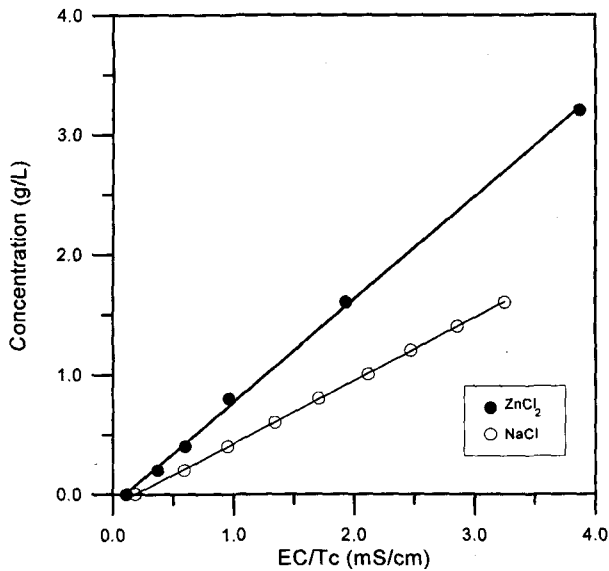


Figure 2. Relationship between electrical conductivity and concentrations of NaCl and ZnCl₂ solutions. Tc denotes

obtained from the lower range to calculate the retardation factor given by Eq. (1b) since the concentrations of ZnCl₂ in the BTC corresponded to that range. The moisture content, being equivalent to porosity under the saturated condition, that is necessary to calculate the retardation factor, was obtained from the TDR measurement. The bulk density, ρ_b , was 1.93 estimated from the moisture content, θ , being equal to 0.27 and specific density of the soil particles which was assumed to be 2.65 g/cm³.

Transport parameters of BTCs such as advection coefficient (V) and dispersion coefficient (D) were also estimated from Eq. (2) using CXTFIT code (Parker and van Genuchten, 1984) which is based on nonlinear least-squares inversion method. With the parameters of NaCl BTC and the retardation factor, R, calculated from the K_d , we predicted the BTC of ZnCl₂ and compared with the measured BTC of ZnCl₂. We also estimated the V, D and R of ZnCl₂ BTC simultaneously and compared with those of NaCl. In addition, with the parameters of V and D obtained from the NaCl BTC, we estimated the decay coefficient in Eq. (2) for Zn assuming that the transfer of Zn ions from the aqueous phase to the solid phase by sorption due to ion exchange or precipitation can be considered to be an irreversible process.

Results and Discussions

The result of retardation factor calculated from the K_d coefficient is given in Table 1. The K_d , fitted with the linear adsorption isotherm model, was 333 mL/g and 17 mL/g for the lower and higher concentration ranges respectively. The

Table 1. Distribution coefficients and retardation factors of the studied sandy soil (pH=6.95~8.15)

Range	C_i (mg/L)	C_{eq} (mg/L)	C^* (μ g/g)	K_d (mL/g)	ρ_b (g/cm ³)	θ	R
Lower	4.9	0.2	46.5	333	1.93	0.27	1633.9
	43.3	1.6	417.1				
	401.8	11.9	3898.4				
Higher	401.8	11.9	3898.4	17	1.93	0.27	121.8
	2646.0	858.9	17871.0				

(C_i : initial concentration of Zn in solution, C_{eq} : equilibrium concentration of Zn in solution, C^* : amount of Zn sorbed per dry weight of soil).

retardation factor, R, was 1633.9 and 121.8 for each concentration range. The higher R for the lower concentration range was due to the higher K_d that can be explained by a sharp increase in the adsorbed amount of Zn ion as the initial concentration increases. These results are comparable with the results of Roy *et al.* (1987) who conducted a batch test and obtained the K_d of lead for Cecil clay loam with 232 mg/L. The pH in their test was 4.5 and the upper limit of equilibrium concentration, C_{eq} , was 1 mg/L whereas the pH in our test was between 6.95 and 8.15 and that of C_{eq} was 11.9 mg/L for the lower concentration range. Rather good agreement between K_d values of 232 and 333 can be found by the fact that the lower pH used in their test was compensated with the higher C_{eq} in our test since the K_d increases with pH but decreases with C_{eq} although the heavy metal elements used in the batch tests were different in their adsorptive capacities.

Figure 3 shows the result of NaCl BTCs calibrated for effluent concentrations monitored using the EC-meter and fitted with the analytical solution (Eq. (2)) of convection-

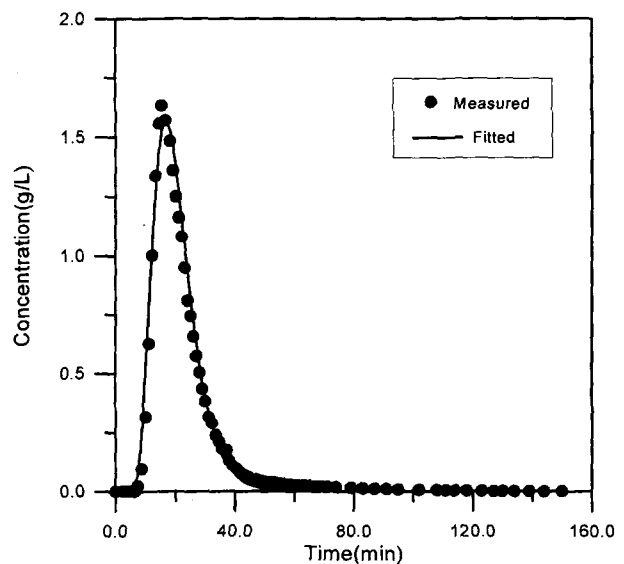


Figure 3. The measured breakthrough curve (BTC) of NaCl and the fitted with CDE model with R=1.

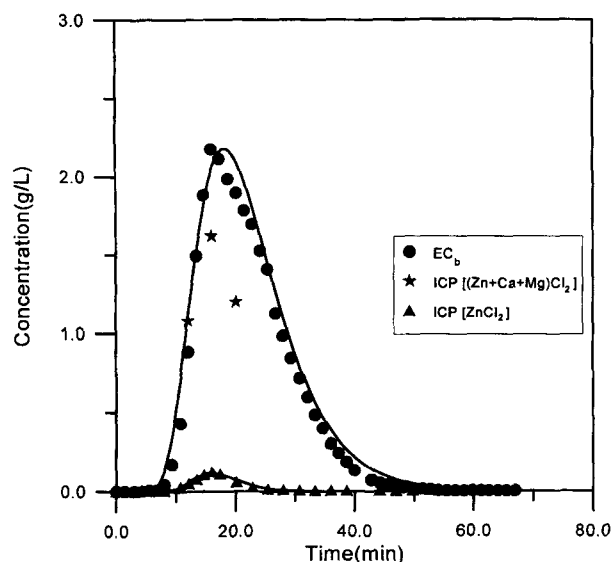


Figure 4. Various forms of BTCs for different analysis of effluents.

dispersion equation. The peak concentration decreased to 15% of the input concentration at the travel distance of 20 cm. The peak was observed at approximately 16 min. The BTCs of $ZnCl_2$ solution are shown in Figure 4. The peak of $ZnCl_2$ BTC data detected by ICP was far less than that of bulk electrical conductivity (EC_b) BTC data measured by the EC-meter, but the travel times of the peak concentrations were more less the same. Inclusion of other cations (Ca, Mg) concentration in the Zn analysis approached nearly 75% of the BTC measured by the EC-meter. The large difference in the effluent concentrations can be explained by either sorption process caused by ion exchange or precipitation of Zn as a zinc hydroxide form, $Zn(OH)_2$ and possibly by a combined process. It is evident that the cations of Ca and Mg in the soil particles were replaced by Zn since Zn has more ion exchange capacity than the others (Allen *et al.*, 1996), and this was confirmed by the increase of effluent concentration with the account of Ca and Mg ions in the Zn concentration. The possibility of precipitation can be found by the fact that dissolved percent of Zn in water is about 20% at pH 7.0 and decreases up to 0.0 at pH 8.0 (Boyles, 1974). This indicates that about 90% of injected Zn could be possibly precipitated as $Zn(OH)_2$ since the pH of the effluents ranged from 7.3 to 7.9 during the column test.

Comparison of $ZnCl_2$ and NaCl BTC is shown in Figure 5. Note that the peak travel time was nearly identical for two tracers but the magnitude of peak concentration for $ZnCl_2$ was about 15 times less than that for NaCl. This indicates that the retardation effect recognized as a common process existing in heavy metal tracers does not occur in the studied soil for the pH range of 7.3~7.9. The relatively small

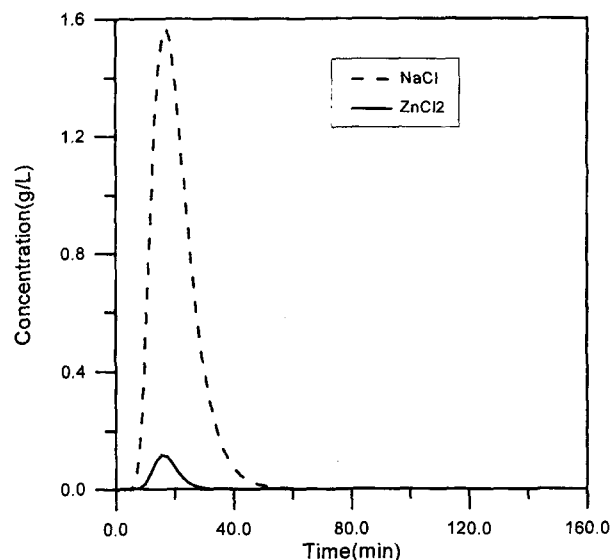


Figure 5. Comparison of the fitted BTCs for NaCl and $ZnCl_2$ tracers.

amount of $ZnCl_2$ detected in the effluent is attributed to the irreversible mass transfer from the aqueous phase to the solid particle interface. The irreversibility of Zn ion can be explained by the experimental condition in which no opportunity for Zn ion to desorb from the particle interface was given because the tap water used as a leaching fluid during the steady state condition to push down the Zn tracer had very low electrolyte concentration without any heavy metal element stronger ion exchange capacity than Zn.

Transport parameters estimated using the analytical solution (Eq. (2)) of CDE model are presented in Table 2 for various cases of optimization condition. In case 1, we assumed that

Table 2. Estimated transport parameters of NaCl and $ZnCl_2$ BTCs when fitted with CDE model. NA denotes not available. (V: cm/min, D: cm^2/min)

Case	Optimization condition	Estimated parameters	NaCl	$ZnCl_2$	Remark
1	R=1 $\mu=0$	V	1.098	NA	
		D	1.128	NA	
2	R \neq 1	V		NA	
		D		NA	
3-1	R=1	V		1.066	
		D		0.654	
3-2	R=1 $\mu\neq 0$ V=1.098 D=1.128	μ		0.2202	From NaCl
		V		149.7	
		D		90.8	
4	R \neq 1 $\mu\neq 0$	R		140.2	
		μ		27.67	
		V			

the NaCl tracer does not show any retardation effect but the $ZnCl_2$ tracer does with the retarded transport parameters of V_R and D_R . The result of fitting to the measured $ZnCl_2$ BTC, however, was very poor yielding unrealistic values of V and D . For case 2 where we assumed that retardation occurs but decay does not occur, optimization of parameters failed as well to fit the $ZnCl_2$ BTC. The results of case 1 and 2 for $ZnCl_2$ indicate that under the measured $ZnCl_2$ BTC retardation effect on the transport parameters can not describe properly the mobility of Zn ion because any value of R larger than 1 would result in a delayed peak of the BTC that is greatly different from the measured BTC.

Accommodation of the decay coefficient (case 3 and 4) gave reasonable fittings to the measured BTC. In case 3, we assumed no retardation ($R=1$) with the occurrence of decay process ($\mu \neq 0$) in which case 3-1 optimized V , D and μ whereas case 3-2 optimized only μ with the fixed V and D obtained from the NaCl fitting. The optimized values of μ resulted in a nearly identical one for both cases implying that the absolute decrease of $ZnCl_2$ compared to the NaCl BTC can be only described by the decay coefficient. It is noted that the case 4 of optimizing all the parameters gave rather high values of V , D and μ compared to those values of case 3-1. The magnitude of the increase for the three parameters approximately coincides with the increased value of R with 140.2. The results of case 4, however, can be considered to be incorrect in terms of R value since the measured $ZnCl_2$ BTC did not show any retardation effect. Similar results for case 1 and case 3-1 of the estimated V and D parameters also imply that the decay coefficient used in case 3 can correctly reflect the transport behavior of $ZnCl_2$ in

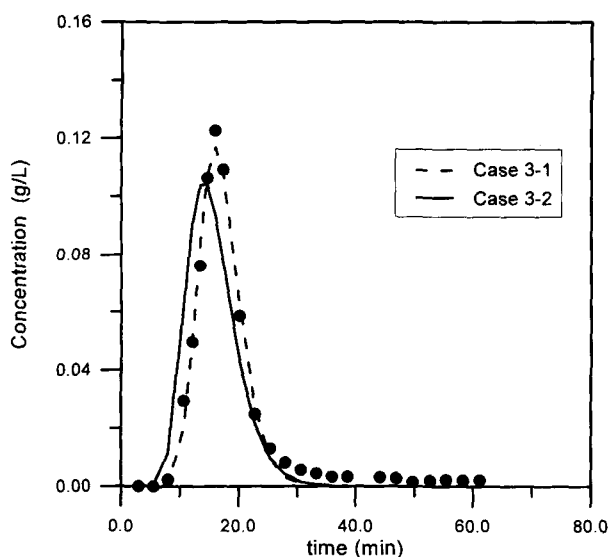


Figure 6. Fitted BTCs to the measured $ZnCl_2$ BTC data with a decay coefficient in the CDE model. Case 3-1 is V , D , μ fitting. Case 3-2 is μ fitting with V , D from NaCl fitting. In each case, retardation factor was 1.

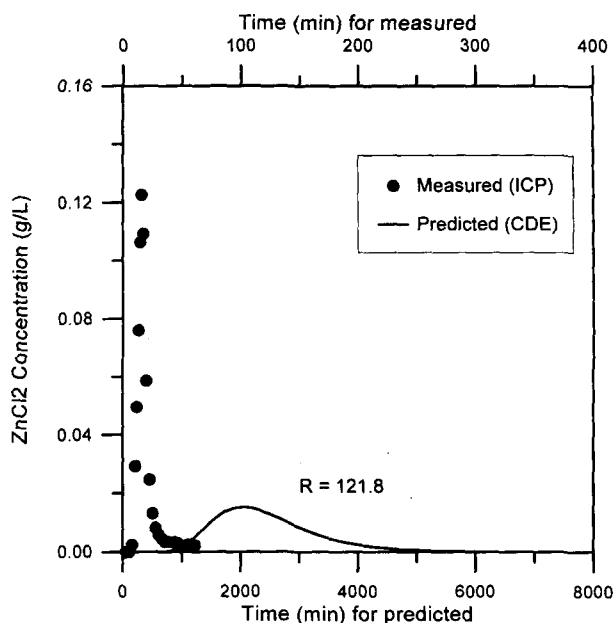


Figure 7. Predicted BTC of $ZnCl_2$ with retardation factor and measured BTC.

the studied soil. The fitted curves to the measured data for case 3 are shown in Figure 6.

Based on the R value calculated from the K_d , and V and D of NaCl tracer, we predicted the $ZnCl_2$ BTC. Comparison of the measured $ZnCl_2$ BTC with the predicted is shown in Figure 7. The predicted BTC yielded a different shape from the measured BTC in terms of peak concentration and travel time of the peak concentration. In this regard, the theory based on the retardation effect failed to describe the transport of Zn ion showing a strong ion exchange capacity. Hence under the pH of 7.3 to 7.9 where most of Zn precipitates or is sorbed onto the solids particles interface, transport of the $ZnCl_2$ solution can be predicted using the CDE model accommodating the decay coefficient that reflects the irreversible decrease of Zn in aqueous phase rather than the retardation coefficient.

Conclusion

In order to investigate the existence of retardation effect of Zn ion in a sandy soil, we conducted batch and column tests using a standard procedure and a breakthrough concept under a steady state condition. The BTC of Zn showed about 20 times low peak compared to the total concentration as measured by the EC-meter. The large difference was due to the strong ion exchange capacity inherent in Zn ion over other cations such as Ca and Mg, coupled with the precipitation of Zn as a hydroxide form under the relatively high pH range (7.3~7.9) used. Use of a retardation factor calcu-

lated from the distribution coefficient determined by batch test with the transport parameters (V and D) of conservative solute, NaCl, could not describe properly the $ZnCl_2$ concentration in terms of the peak concentration and travel time of the peak concentration. Hence, the commonly accepted retardation effect caused by adsorption process of heavy metals was not present enough to describe the transport behaviour of Zn ion since desorption of Zn ion could not be realized under the BTC condition. Rather, accommodation of a decay coefficient was more appropriate to realize the transport behaviour of Zn under the pH condition used in this study.

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