

## TDR을 이용한 사질토양에서의 중금속 이동 추정

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## Predicting Migration of a Heavy Metal in a Sandy Soil Using Time Domain Reflectometry

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### ABSTRACT

Recently, transport parameters of conservative solutes such as KCl in a porous medium have been successfully determined using time domain reflectometry (TDR). This study was initiated to investigate the applicability of TDR technique to monitoring the fate of a heavy metal ion in a sandy soil and the distribution of its concentration along travel distance with time. A column test was conducted in a laboratory that consists of monitoring both resident and flux concentrations of  $ZnCl_2$  in a sandy soil under a breakthrough condition. A tracer of  $ZnCl_2$  (10 g/L) was injected onto the top surface of the sample as pulse type as soon as a steady-state condition was achieved. Time-series measurements of resistance and electrical conductivity were performed at 10 cm and 20 cm of distances from the inlet boundary by horizontal-positioning of parallel TDR metallic rods and using an EC-meter for the effluent exiting the bottom boundary respectively. In addition, Zn ions of the effluent were analyzed by ICP-AES. Since the mode and position of concentration detected by TDR and effluent were different, comparison between ICP

analysis and TDR-detected concentration was made by predicting flux concentration using CDE model accommodating a decay constant with the transport parameters obtained from the resident concentrations. The experimental results showed that the resident concentration resulted in earlier and higher peak than the flux concentration obtained by EC-meter, implying the homogeneity of the packed sandy soil. A close agreement was found between the predicted from the transport parameters obtained by TDR and the measured  $ZnCl_2$  concentration. This indicates that TDR technique can also be applied to monitoring heavy metal concentrations in the soil once that a decay constant is obtained for a given soil.

**Key words** : Heavy metal, Time Domain Reflectometry (TDR), Breakthrough curve (BTC), Convection-dispersion Equation (CDE) model, Decay constant

## 요 약 문

최근 들어, 다공질 매질에서의 KCl 같은 보존성 용질의 운송계수를 결정하는데 TDR이 성공적으로 사용되고 있다. 본 연구는 TDR 기법이 사질 토양에서 중금속 이온의 운명과 시간에 따른 농도 분포를 측정하는데 적용가능성을 알아보기 위하여 수행되었다. 실험실에서 파과곡선 조건의 주상실험을 수행하여 사질토양에서 침출수와 잔존수의  $ZnCl_2$  농도를 측정하였다. 정상류 상태에서 추적자인  $ZnCl_2$  (10g/L)를 토양시료 상부에 순간주입한 후, 시간별로 토양시료 상부로부터 각각 10cm와 20cm 깊이에서 수평으로 설치된 TDR 탐침을 이용하여 저항을, EC-meter를 이용하여 침출수의 전기전도도를 측정하였고, 침출수의 Zn 이온의 농도는 ICP-AES를 이용하여 분석하였다. TDR과 침출수로부터 구한 농도측정 방법이 다르기 때문에, ICP-AES로부터 구한 농도와 토양시료 상부로부터 10 cm에서 TDR로 측정된 잔존수 농도로부터 구한 운송파라미터를 감쇄상수를 고려한 CDE 모델에 적용하여 구한 침출수 농도와 비교하였다. 실험결과에 의하면, 잔존수의 침투농도는 EC-meter로 측정된 침출수의 것보다 더 빨리 그리고 더 높게 나타나 사질 토양이 균질한 것으로 나타났다. TDR로 구한 운송 파라미터로부터 추정된  $ZnCl_2$ 의 농도와 ICP-AES로 측정된 농도는 상당히 일치했다. 이것은 주어진 토양에서 감쇄상수를 얻기만 하면 TDR 기법이 특정깊이에서의 중금속의 침출수 농도를 측정하는데에도 적용가능하다는 것을 의미한다.

**주제어** : 중금속, 시간영역 광전자파 분석기, 파과곡선, CDE 모델, 감쇄상수

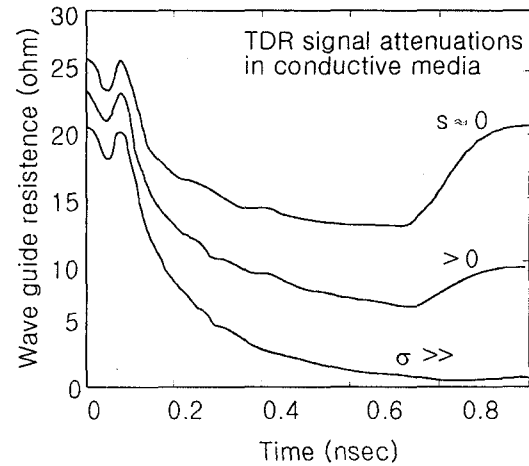
## Introduction

Dispersion of heavy metals becomes one of

the key issues related to environmental hazard caused by various industrial activities. Diagnostic pathways of toxic

heavy metals are air, water, sediments and soils in which the most vulnerable is the soil environment as it has direct contact with their source and becomes the first acceptor when they start to mobilize. In order to carry out a proper remedial action, it is a prerequisite to delineate the scope and degree of contamination. To meet this, prediction of the fate of heavy metals in a porous medium becomes an essential tool. Accurate prediction depends on the selection of transport models and accompanying transport parameters that should be predetermined. Determination of the parameters has been done extensively using laboratory breakthrough experiment in which various monitoring techniques can be used.

Recently, time domain reflectometry has been proved to be a viable technique for monitoring conservative solutes such as  $\text{CaCl}_2$ ,  $\text{KCl}$ ,  $\text{NaCl}$  in a porous medium. A number of researches were successfully conducted to obtain the breakthrough curves and consequently the solute transport parameters<sup>1,2,4,9,13)</sup>. They used the principle of changes in resistance of reflected electromagnetic waveform representing the conductance of porous medium surrounding the TDR probes as the concentration of solutes changes. When the concentration of solutes increases, resistance of the waveform decreases (Fig. 1). Therefore, a calibration procedure is required to convert the resistance expressed in Ohm to the normal concentration. Several researches



**Fig. 1. TDR signal output from parallel rod electrodes in media of low, moderate and extreme electrical conductivities (after Dalton and van Genuchten, 1986).**

were conducted to investigate the relationship between concentration of solute and resistance<sup>3,7,10,11)</sup>. Application of TDR to monitoring the resident concentration of a conservative solute was extensively conducted at both field<sup>5)</sup> and laboratory<sup>6)</sup> scales using horizontally-positioned TDR probes. However, all of the studies were conducted using the tracer as conservative solutes. Since in general, the TDR can detect solutes containing inorganic chemicals contributing to the conductance of the porous medium, solutes made of heavy metals can also be detected. The previous study of Kim et al. (1998b)<sup>8)</sup> has shown that the most important factor related to the migration of a heavy metal ion in a soil was a decay constant representing an irreversible

sorption caused by ion exchange between solution and solids particle. Hence, in this study, we made an attempt for monitoring flux concentrations of heavy metal solution ( $ZnCl_2$ ) in a sandy soil using TDR-measured resident concentration by incorporating a decay constant accounting for a sorption process of Zn ion, and compared with flux concentration of  $ZnCl_2$  analyzed with ICP.

## Materials and Methods

### 1. BTC experiment

A soil column was constructed by packing soil materials collected from a river into a PVC cylinder with 20 cm in both diameter and height. The soil was classified as a sandy soil which is the same type as Kim et al. (1998b)<sup>8)</sup> studied. The particle size analysis is given in Fig. 2. Parallel TDR

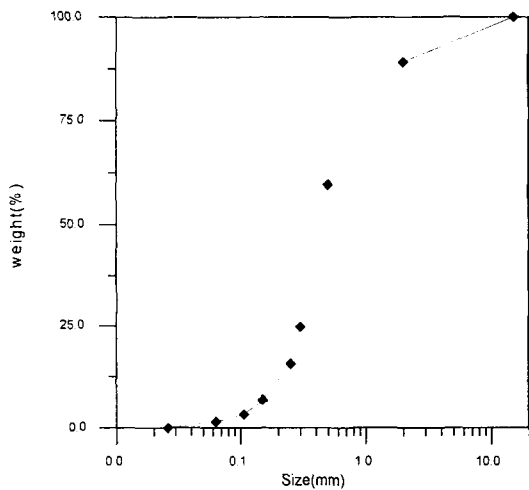


Fig. 2. Particle size distribution of the sandy soil.

metallic rods with a spacing of 20 mm and the length of 150 mm were horizontally positioned at the middle of the sample. A steady-state condition was imposed on the sample by applying a constant head of tap water containing about 0.2 mS/cm of electrical conductivity (EC) at the top using a Mariotte system while the Darcian flux exiting the bottom boundary (Fig. 3) was measured with time. The steady-state condition was confirmed by measuring the constant flux after some time elapsed. After the steady-state condition had been achieved, 314 mL of  $ZnCl_2$  solution with the concentration of 10 g/L was injected on the top surface with a pulse duration of  $t_0 = 2.87$  min upon completing the infiltration of

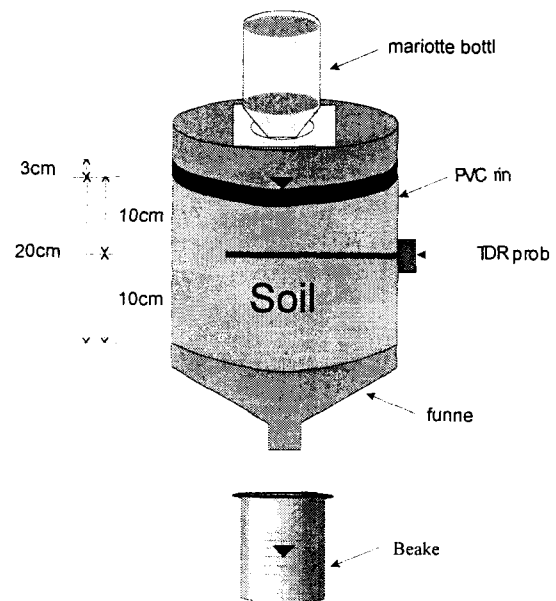


Fig. 3. Experimental set-up for permeability test using constant head method and determination BTC.

the ponded water. Resistance of bulk soil surrounding the TDR probe and electrical conductivity of effluent were measured with time by means of cable tester (Tektronix 1502B) connected to the TDR probe via coaxial cable and an EC-meter respectively as soon as the tracer was injected. Chemical analysis was also performed to obtain information on the cations present in the effluent using ICP-AES.

## 2. Calibrations

Calibrations were needed to derive actual concentration  $C$  (g/L) from either electrical conductivity measured by EC-meter or resistance measured by TDR cable tester. The former is straight forward and consists of a series measurement of electrical conductivities (mS/cm) for several solutions made by dissolving incrementally a certain amount of  $ZnCl_2$  into the tap water. The relationship between  $C$  and EC for the range of 0 to peak concentration obtained from BTC experiment is shown in Fig. 4.

For TDR calibration, we used pulse input method (PIM)<sup>15)</sup>. The method is based on the calibration coefficient relating resistance to input concentration by :

$$\beta = \frac{c_0 t_0}{\int_0^t \left[ \frac{1}{R(t)} - \frac{1}{R(t_i)} \right] d\tau} \quad (1)$$

where  $\beta$  is the calibration coefficient, and  $C_0$ ,  $t_0$  are the concentration and duration of solute pulse, and  $R(t)$ ,  $R(t_i)$  are the

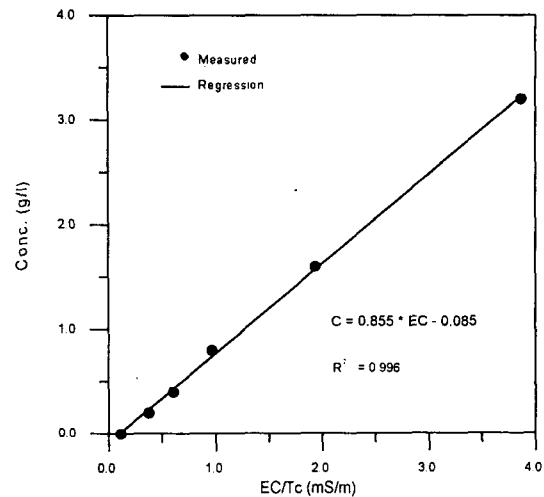


Fig. 4. Relationship between  $C$  (g/L) and EC (mS/cm) for  $ZnCl_2$  solution.

resistance measured at time  $t$  and before application of solute pulse, and  $\tau$

is a dummy variable for time integration. Then the concentration at time  $t$  can be given by :

$$C(t) = \beta \cdot \left[ \frac{1}{R(t)} - \frac{1}{R(t_i)} \right] \quad (2)$$

The theoretical background of this method lies on the fact that all solutes injected during the application time,  $t_0$ , is detected by TDR as changes in resistance during breakthrough assuming that there exists a complete mass recovery. Thus the ratio of input concentration ( $C_0$ ) times duration of pulse ( $t_0$ ) and numerical convolution of the inverse of resistance with time gives the calibration coefficient. Since we used a sandy soil uniformly packed in a PVC cylinder, use of this method in our

**Table 1. Probability density functions of CDE model for two different concentration modes (Kim, 1996)**

Modes	Probability density functions
Flux	$f(z, t) = \frac{z}{2\pi Dt} \text{Exp} \left[ -\frac{(z - Vt)^2}{4Dt} \right]$
Resident	$f(z, t) = \frac{V}{\pi Dt} \text{Exp} \left[ -\frac{(z - Vt)^2}{4Dt} \right]$ $-\frac{V^2}{2D} \text{Exp} \left( -\frac{Vz}{D} \right) \text{Erfc} \left[ \frac{z + Vt}{4Dt} \right]$

studied soil was considered to be appropriate.

### 3. Data analysis

The BTC data obtained through the measurement of resident and flux concentrations form the time-series concentration for each fixed position. Parameters describing the migration of  $\text{ZnCl}_2$  were obtained by fitting a well known transport equation, namely, convective-dispersive equation (CDE), given in the form of probability density function (pdf), to the measured BTCs. Those pdfs are given in Table 1.

Transport of reactive chemicals showing retardation and decay or degradation in an one dimensional soil system can be described by the following equation<sup>12)</sup>:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} - \mu C \quad (3a)$$

$$R = + \frac{\rho_b}{\theta} K_d \quad (3b)$$

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,  $\mu$  is first-order decay constant, t is time, x is distance,  $\rho_b$  is bulk density,  $\theta$  is porosity and  $K_d$  is distribution coefficient.

The analytical solution of Eq. (3a) for flux concentration in case of pulse type injection of tracer was given by van Genuchten and Alves (1982)<sup>14)</sup> using appropriate initial and boundary conditions for finite length of a porous medium:

$$i) C(x, t) = C_0 \cdot B(x, t) \quad (0 < t < t_0) \quad (4a)$$

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

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

$$ii) C(x, t) = C_0 B(x, t) - C_0 B(x, t - t_0) \quad (t > t_0) \quad (4b)$$

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

Comparison of resident concentration with flux concentration monitored by either EC-meter or ICP was not possible, since the monitoring depth was not identical. Therefore, we predicted the flux type concentration at 20 cm depth using the CDE model given by Eq.(4a) and Eq.(4b) with parameters obtained from the resident BTC at 10 cm depth. The decay constant,  $\mu$ , was obtained by fitting the CDE model to the BTC data of  $ZnCl_2$  measured by ICP with the transport parameters,  $V$  and  $D$ , obtained through the BTC of EC-meter measurement. The retardation factor,  $R$ , was fixed to 1 for the prediction of  $ZnCl_2$  flux concentration because no retardation effect was found for the Zn ion in the studied soil<sup>8)</sup>. This is based on the assumption that those parameters represent the physical properties of the soil, and the effluent concentration detected by EC-meter is of conservative nature since the total concentration was preserved and only Zn ions were sorbed on the particle surface by ion exchange process<sup>8)</sup>. Then the measured flux BTC from ICP was compared with the predicted flux BTC.

## Results and Discussions

Monitored resident (TDR) and flux (EC-meter) BTCs and parameters fitted to the curves are shown in Fig. 5. Resident concentration shows earlier and higher peak than flux concentration implying the homogeneity of the sandy soil with the absence of preferential flow channel. The peak concentration decreased almost by half while more spreading occurred from 10 cm to 20 cm travel distance from the inlet boundary.

Comparison of ICP data on  $ZnCl_2$  with data obtained by EC-meter for flux concentration showed a large difference in the peak concentration although the travel times of the peak concentrations coincide (Fig. 6). It appears that desorption process of Zn did not occur due to addition of tap

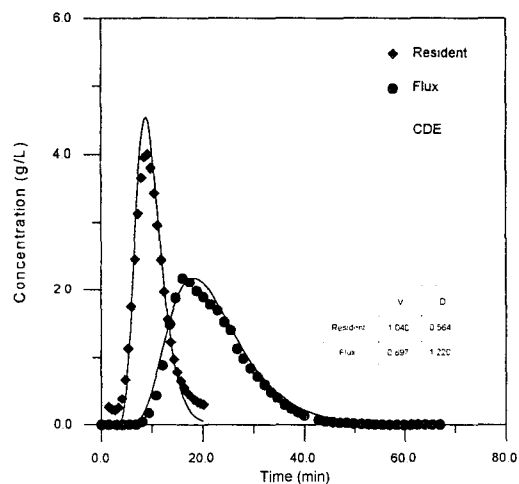


Fig. 5. BTCs monitored by TDR (resident concentration) and EC-meter (flux concentration) and transport parameters of  $ZnCl_2$  solution.

water with lower EC during the breakthrough curve condition, and only decrease of Zn in solution phase occurred. One of the possible explanation for the difference is an ion exchange process, that is an irreversible sorption, between Zn and other cations having less exchange capacity. When the bulk concentrations including cations such as Ca, Mg in the effluent detected by ICP were compared with the EC-meter data, the peak concentration approached nearly 70 % of that of the EC-meter data. This indicates that most of Zn ions is exchanged during migration through pores between solid particles and only 5 % of Zn ions is transported downwards.

Fig. 7 shows the result of fitting the CDE model to the ICP-measured  $ZnCl_2$  concentration to obtain the decay constant with fixed V and D parameters determined

from the BTC of EC-meter measurement. The transport parameters of V and D for the effluent concentration were  $0.897\text{cm min}^{-1}$  and  $1.220\text{cm}^2\text{ min}^{-1}$ . The decay constant,  $\mu$ , was estimated  $0.190\text{min}^{-1}$  indicating that 19% of  $ZnCl_2$  concentration per minute is sorbed on the solids particle surface.

The predicted concentration from the transport parameters (V, D) obtained by TDR and the decay constant showed a good agreement with the  $ZnCl_2$  concentration measured by ICP (Fig 8). The peak concentration and travel time of the peak for the measured and predicted  $ZnCl_2$  were exactly identical indicating an appropriateness of predicting flux type heavy metal concentration by TDR measurement. It appears that although the TDR can not directly monitor the flux type

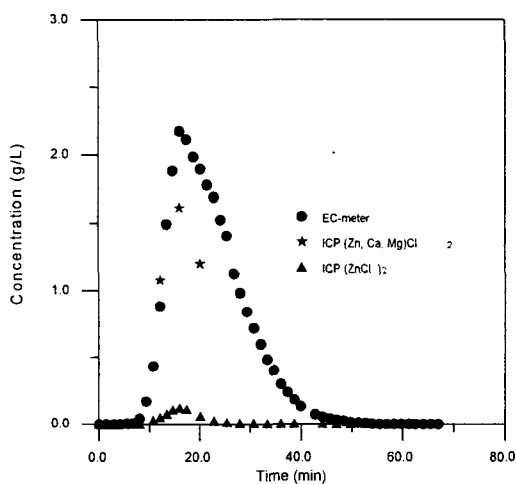


Fig. 6. Comparison of BTC data as measured with ICP and EC-meter.

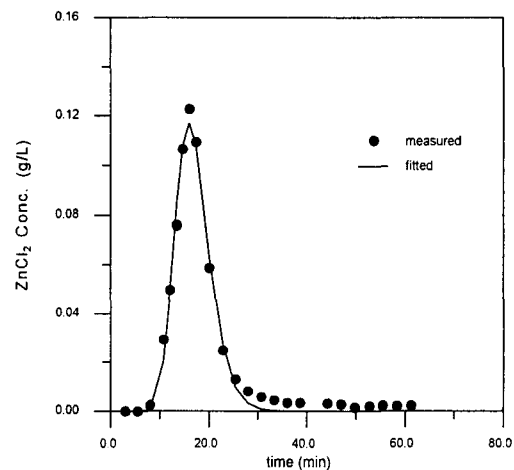


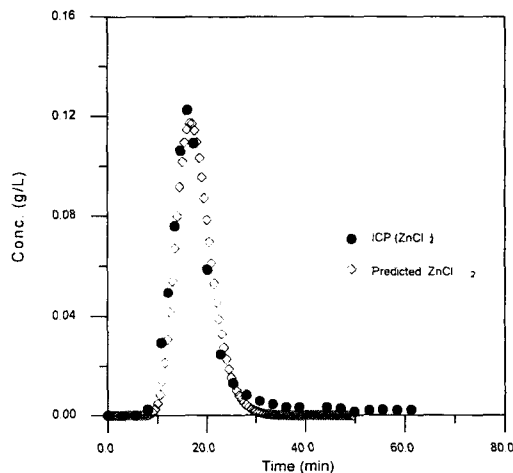
Fig. 7. Fitting of CDE model to the  $ZnCl_2$  BTC data measured by ICP to obtain the decay constant.



of  $ZnCl_2$  concentration at a certain depth of a soil, a decay constant representing the sorption process of Zn can help the TDR technique to monitor the migration of an heavy metal in the soil. Therefore, TDR technique can be applied to monitoring the fate of a heavy metal ion in a sandy soil as long as the decay constant is obtained by the ICP analysis for that soil.

### Conclusions

We performed a breakthrough experiment using  $ZnCl_2$  solution as a tracer to investigate the applicability of TDR



**Fig. 8.** Comparison of BTC data as measured with ICP and the predicted flux concentration using CDE model accommodating a decay constant with the transport parameters obtained from TDR ( $V = 1.040$ ,  $D = 0.564$ ,  $\mu = 0.19$ ).

technique to monitoring migration of a heavy metal ion in a sandy soil. Time-series data of the  $ZnCl_2$  concentration were monitored using TDR at 10 cm depth and an EC-meter at 20 cm depth. The effluent concentration as a flux type collected at 20 cm depth corresponding to the exit boundary was analyzed for Zn with ICP-AES. Results showed that the peak  $ZnCl_2$  concentration of ICP data yielded only 5 % of the EC-meter data. Inclusion of bulk concentration in the form of  $CaCl_2$  or  $MgCl_2$  to the ICP data approached nearly 70 % of the EC-meter data indicating that most of the Zn ions was exchanged during migration in the soil. However, the predicted concentration from the transport parameters obtained by TDR and a decay constant obtained by BTC of Zn ion showed a good agreement with the  $ZnCl_2$  concentration measured by ICP. Application of TDR technique to monitoring the fate of a heavy metal ion in the landfill site will be promising on the condition that the decay constant can be obtained by the BTC of Zn ion for a given soil sample. Further studies should be conducted with multiple TDR probes installed at various depths in a soil sample in order to increase the predictability of TDR technique.

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