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Electrical Conductivity Breakthrough Curve of Soil Column with Residual Diesel Fuel

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ABSTRACT: In order to demonstrate the applicability of bulk electrical conductivity breakthrough curves for estimating solute transport in soil with residual diesel fuel, electrical conductivity breakthrough curves on column test was investigated. In addition, the electrical conductivity breakthrough curves were compared with Mobile-Immobile Model to verify the amount of solute in the immobile fraction of the pore volume. Changes in the electrical conductivity represented as a relative parameter with time gives information about solute transport in both clean saturated soils and saturated soils with residual diesel fuel. This illustrates the advantage of electrical conductivity BTC to monitor solute concentration continuously with time based on instantaneous electrical measurements. Electrical conductivity BTCs can provide an effective means of qualitative monitoring on solute transport with longitudinal direction of transport.

1 INTRODUCTION

In order to conduct an accurate predition of flow and transport processes, accurate measurement methods and approapriate modelling approaches is necessary. Soil column tests provides a reliable means of evaluating the solute transport characteristics in soil. To provide an effective means of analyzing solute transport in soil medium, a column test device installed with 4-electrode electrical conductivity sensors have been developed(Kim 2009). Detection and monitoring by means of measuring the electrical properties of soils is advantageous in that it can be performed quickly with little data processing needed to obtain accurate and repeatable results (Rinaldi & Cuestas 2002; Oh et al. 2007; Oh et al. 2008). In many cases, contaminants are introduced into the subsurface at concentrations sufficient to alter the electrical properties of soil. The electrical conductivity of saturated soils is a measure of how well a soil-fluid mixture accommodates the transport of electric charge, and is a physical property which changes significantly according to the type and concentration of contaminant present.

The objective of this study is to demonstrate the applicability of bulk electrical conductivity breakthrough curves(BTCs) for estimating solute transport in mixed contaminated soils. The influence of residual diesel fuel, which is NAPL(Non Aqueous Phase Liquid) and non-conductive contaminant, on electrical conductivity breakthrough curves on column test was investigated. The electrical conductivity BTCs were analyzed based on Mobile-Immobile Model (MIM) to verify the amount of solute in the immobile fraction of the pore volume.

2 MOBILE-IMMOBIEL MODEL

Advection-dispersion equation has been adapted for transport of conservative solute in a homogeneous porous medium. However, soils often poses heterogenieties in the pore space, simply from the spatial difference in the soil particle size, composition and the degree of compaction, or even from biological activities which can create large pores with time. Conceptualizing the transport of chemicals in such soils becomes a challenging process. Generally, BTCs from solute transport experiments in heterogeneous media or soils with macropores can be characterized by early breakthrough and tailing, which results in highly asymmetrical shapes. Such phenomenon can be understood in terms of the presence of fast transport through the macropores and diffusion of solute into and out from the less mobile pores.

Dubè et al.(2003) found that soils contaminated by non-aqueous phase liquids(NAPLs) experience such heterogeneities, since NAPLs change the transport by the aqueous phase by changing the network of pores assessable to aqueous flow, namely by creating circuits of pores that by-pass porous zones occupied by residual NAPL. Many other studies (Rao et al., 1980; Nkedi-Kizza et al., 1983; Lee et al., 2000) have shown that MIM model can describe some forms of preferential solute movement.

Transport in soils with macropores can be conceptualized by assuming advective transport in the macropore region and diffusion into or out of the less mobile regions by using a first-order kinetic diffusion process (Coats & Smith, 1964; Van Genuchten & Wierenga, 1976). The model is refered to as physical non-equillibrium, mobile-immobile(MIM) model. In the MIM model, the liquid phase is assumed to be divided into mobile and immobile regions. Advective-dispersice solute transport only occurs in the mobile region, and the movement of solute between the mobile and immobile regions are described as first-order diffusive mass transfer. The two governing equations of the MIM model for conservative solute are as follows.

$$\theta_m \frac{\partial c_m}{\partial t} = \theta_m D_m \frac{\partial^2 c_m}{\partial x^2} - J \frac{\partial c_m}{\partial x} - \lambda(c_m - c_{im}) \quad (1)$$

$$\theta_{im} \frac{\partial c_{im}}{\partial t} = \lambda(c_m - c_{im}) \quad (2)$$

where; θ is the volumetric water content, J is the solute flux, λ is the mobile-immobile first-order diffusive mass transfer coefficient, D_m is the dispersion coefficient for the mobile region, c_m and c_{im} are the resident solute concentrations in the mobile and immobile regions, respectively. Note that θ is equal to $\theta_m+\theta_{im}$, the sum of the volumetric water content corresponding to mobile and immobile regions, respectively. Parameter β is used to describe the fraction of mobile region, equal to the ratio between mobile and total porosity($\beta=\theta_m/\theta$). Solution to Equations (1) and (2) can be obtained by substituting appropriate inlet and outlet boundary conditions.

3 TEST METHOD

3.1 *Column test device*

Sensor for measuring electrical conductivity was designed to be composed of 4 electrodes with the geometry (or curvature) following the inner wall of the column test. Since the current drawn through the measurement electrodes is very small on the four-electrode array, there is no appreciable buildup of ions at the electrodes and it can operate at very low frequencies without being polarized. In addition, electrode geometry following the inner wall of the column allowed avoiding sample disturbance. The design follows the basics of the four-electrode measurements but the array is directed parallel to the direction of solute transport. Each fan-shaped electrode has a thickness of 2mm; such design ensured sufficient area of contact between the soil and electrodes. The electrodes are placed 3mm apart, which gives a total of sensor thickness of 17 mm. Figure 1 shows a schematic diagram of fan-shaped 4-electrode measuring sensor and column test device. Three conductivity sensors are located at 58.5mm, 200mm, and 341.5mm away from the influent/effluent boundary. The 400mm long, 50mm diameter column is made of acryl to avoid flow of electrical current between the fan-shaped electrodes. In addition, porous stone of 10mm thickness was placed as a diffuser at the influent and effluent boundaries to induce 1-D flow and minimize disturbance in flow through the boundary.

The three electrical sensors are connected to the 4263B LCR meter (Agilent Technologies, Japan) for conductance measurements via channel selector, specially designed and produced for the developed column test device. The channel selector allows measurements at the three different sensors to be made using a single LCR meter by functioning as an electrical bridge. Since electrical measurements can be conducted instantaneously, measurements on sensors E1~E3 can be made at desired time intervals.

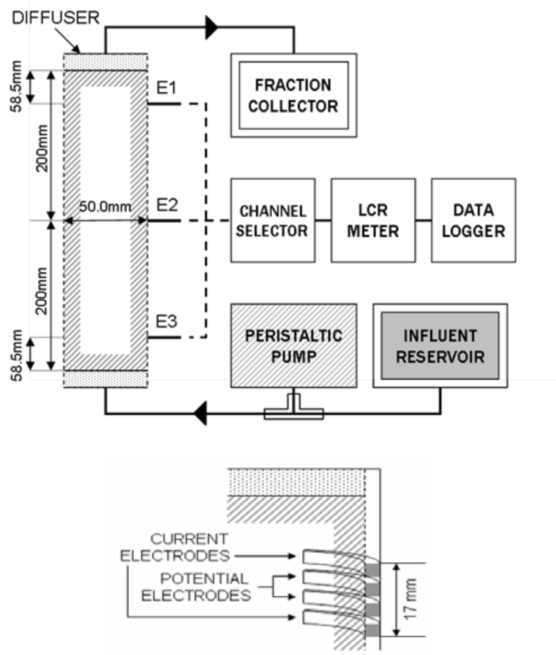


Figure 1. Schematic diagram of the fan-shaped 4-electrode conductivity sensor and column test devices (modified after Kim (2009))

3.2 *Test materials and method*

Silica sand that is commercially available in Korea was used as the material for experimental study. Referred to as Jumunjin sand, it is classified as poorly graded sand(SP) under the Unified Soil Classification System(USCS). The test soils were prepared by washing using deionized water several times prior to oven drying at 100˚C for 24 hours. The soil was thoroughly washed in order to minimize the presence of soluble excess salts which can affect the pore water conductivity. The prepared soil was evenly compacted into four 10cm thick layers into the column. In order to completely saturate the soil columns, CO_2 purging was performed for 2 hours prior to injecting the saturating solution. The high solubility of CO_2 gas into water enables inter-connected pores to be easily saturated. Complete saturation was assumed in all tests conducted. For solute injection tests on soils, DI water was injected as the solution of saturation using the peristaltic pump. In order to induce steady-state flow condition, injection was maintained for more than 48 hours. Such procedure also contributed to minimizing the excess salt remaining in the soil samples.

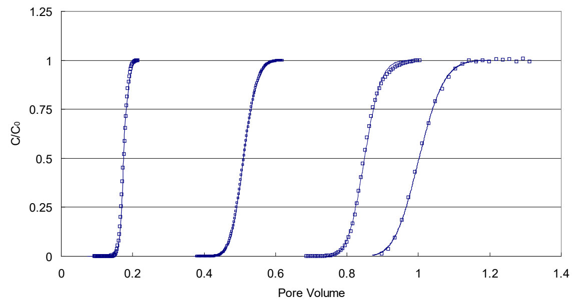
In order to minimize the uncertainties in data analysis, a simple uniform 1-D steady state solute flow was simulated by injecting non-reactive solute into soil columns. To obtain the solute BTC at the exit boundary, solute samples were collected by using a fraction collector in minute intervals dependent on the volumetric discharge rate. Verification was conducted by comparing the electrical conductivity BTC to the conventional BTC obtained from chemical analysis of effluent samples.

In tracer injection tests on soils contaminated by residual diesel, diesel fuel was trapped in the soil column similar to several methods reported in the literature (Pennell et al., 1993; Dawson & Roberts 1997; Fortin et al., 1998; Dubè et al., 2002). Diesel fuel dyed using Sudan IV was introduced into a soil column at a rate of 0.3 mL/min. Diesel fuel injection was followed by DI water injection at 0.6 mL/min to displace the diesel. Such process continued until no free diesel was collected at the effluent. Note that the diesel was injected and displaced at a high flow rate relative to that of tracer injection test. High rate of diesel injection was aimed at minimizing fingering of the displacement front from the difference in viscosity between DI water and diesel. A possibility of irregular displacement front which may produce undisplaced lenses of diesel was visually verified. In addition, a high rate of flow selected for displacing free diesel was designed to avoid displacement of free diesel during tracer-injection tests which were conducted at a flow rate of 0.3 mL/min.

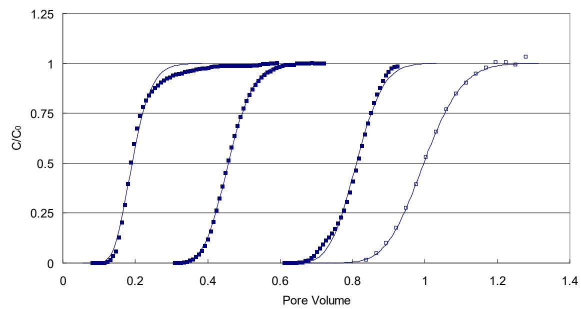
4 RESULTS AND ANAYSIS

In order to investigate the influence of residual diesel on water flow, Figures 2 and 3 show the BTCs obtained from column tests. BTCs shown as solid lines were fitted BTCs by least-squares analysis and transport parameters were estimated by using the CXTFIT code. The saturation degree of diesel fuel in soil column was about 23.1%. Note that the BTCs are results obtained from identical volumetric discharge. Relative concentrations are plotted against the effective PV time units for a simple comparison. Note that the 1 pore volume for clean sand was 1,059 minutes while that of diesel-contaminated sand was 816 minutes based on effluent BTCs(c(x,t)=0.5). Such values indicate 22.95% acceleration for breakthrough due to residual diesel, are in good accord with the residual diesel saturation of 23.08%. The amount of accelerated breakthrough computed based on bulk soil conductivity BTCs were 17.22%, 31.39%, and 25.94% for sensors E3, E2 and E1, respectively. The amount of accelerated breakthrough is similar for effluent BTC and E1 BTC. However, values from sensors E2 and E3 indicate possibilities of heterogeneity in with depth. Again, such results demonstrate the applicability of multiple BTCs for 2-D analysis. Tendency of earlier breakthrough, tailing and asymmetrical shape is clear in the results of pulse injection tests. These characteristics are usually recognized as indications of heterogeneous flow characterized by a rapid preferential flow through a small fraction of the pore volume (Reedy et al. 1996). Preferential flow is usually related to structural heterogeneities in soil such as interaggregate regions and discrete macropores (Bouma et al. 1977).

The hypothesis of heterogeneous flow is also supported by the inadequacy of the advection-dispersion equation to fit the experimental data. As shown in Figure 4, mobile-immobile representation was found to be more adequate in fitting the experimental data shown in Figure 3(b), especially for effluent BTC. Effluent BTC indicated a significant amount of immobile water fraction at a high mobile-immobile diffusive mass transfer coefficient. Results suggest that the mobile phase was rapidly conducted through the flow domain producing earlier breakthrough and solute remaining in the immobile phase produced tailing of the breakthrough curve.

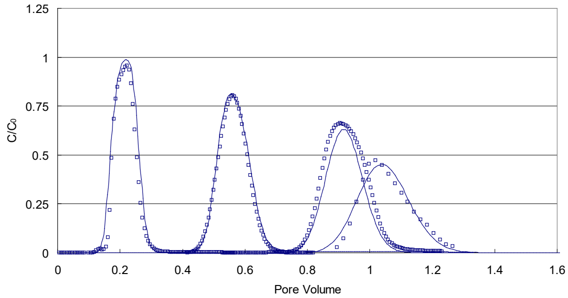


(a) clean soil

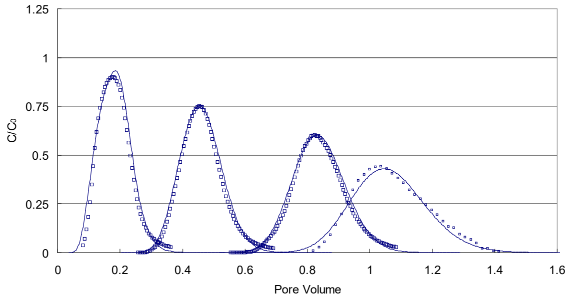


(b) soil with residual diesel fuel

Figure 2. Breakthrough curves obtained from continuous tracer injection test



(a) clean soil



(b) soil with residual diesel fuel

Figure 3. Breakthrough curves obtained from pulse tracer injection test

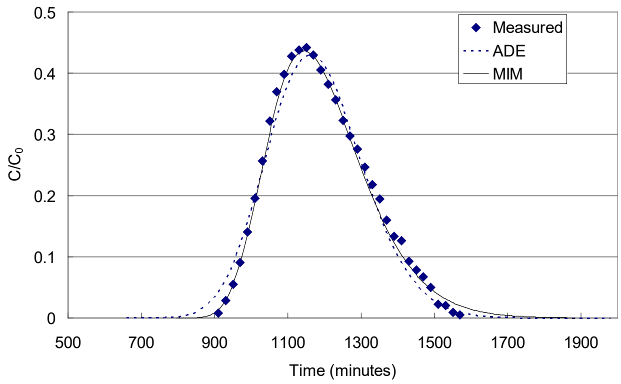


Figure 4. Regression of experimental data on diesel-contaminated soil into MIM model

5 CONCLUSIONS

The electrical conductivity BTC provides an economical and time-effective means of analyzing solute transport through soil since it can be obtained without efforts required in sampling and analysis.

Changes in the electrical conductivity represented as a relative parameter with time gives information about solute transport in both clean saturated soils and saturated soils with residual diesel fuel. This illustrates the advantage of electrical conductivity BTC to monitor solute concentration continuously with time. Electrical conductivity BTCs can provide an effective means of qualitative monitoring on solute transport with longitudinal direction of transport. The hypothesis of heterogeneous flow is also supported by the inadequacy of the advection-dispersion equation to fit the experimental data. The mobile-immobile representation was found to be more adequate in fitting the experimental data.

6 ACKNOWLEDGEMENT

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