

# Determination of the Convective and Diffusive Fluxes from the Transient Profiles of Solute and Solvent under Evaporation Experiment

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## 요 약

토양 속에서 발생될 수 있는 용질과 용매의 복합 수송시스템을 대상으로 한 연구 중 희석상태로부터 포화상태에 이르기까지의 넓은 농도분포를 가지는 토양 용액에 적용될 수 있는 물리화학적 이론에 입각한 지배방정식을 발표한 연구는 전무한 실정이다. 본 연구는 용매와 토양 기체간 그리고 용질과 결정간의 상변화를 고려한 연립물질수지방정식을 제시하고, 여기에 타울적 대류를 포함하는 상호확산 분산수송방정식을 도입하여 대류와 확산에 관한 프릭스를 분리, 결정하는 것을 목적으로 한다.

대류 프릭스의 결정은 타울적으로 이루어지는 것이 이론적으로 타당하며, 이러한 타울적 대류 프릭스가 제공된다면 본 연구에서 제시된 지배방정식을 이용해서 토양용액의 복합수송 시스템을 범용적으로 해석, 예측할 수 있을 것으로 판단된다.

주요어 : convective and diffusive fluxes, complex transport system, mutual diffusion-dispersion equation, heteronomous, simultaneous mass balance equation.

## I. Introduction

Solute and water transport through porous media is a major branch of the environmental impact assessment that most of researchers encounter in the transient zone between salt water and fresh water in coastal aquifers, artificial recharge operations where water of one quality is introduced into aquifers containing water of the other quality, secondary recovery techniques in oil reservoirs where the injected fluid dissolves the reservoir's oil, radioactive and reclaimed

sewage waste disposal into aquifers, the use of tracers such as dyes, electrolytes and radioactive isotopes, in hydrology, petroleum engineering and other scientific and engineering research projects, the use of reactors packed with granular material in the chemical industry, and the movement of fertilizers in the soil and the leaching or accumulation of salts from the soil in agriculture. This problem has been studied by two approaches. In the first approach the porous medium is replaced by a fictitious, greatly simplified, model

in which the mixing that occurs can be analyzed by exact mathematical methods. A single capillary tube, a bundle of capillaries, an array of cells, etc., are examples of such models (e.g., Taylor, 1953; Danel, 1952; Bear and Todd, 1960). The second one, more commonly used currently, is to construct a statistical (conceptual) model of the microscopic motion of the marked fluid particles and to average these motions in order to obtain a macroscopic description of them (Biggar and Nielsen, 1967; Bresler, 1973; Elprince and Day, 1977; van Genuchten, 1980; Parker and van Genuchten, 1984).

The total of dissolved solute in the convection-dispersion model is commonly written as

$$J_u = -D_e \frac{\partial C_u}{\partial z} + J_w C_u \quad (1)$$

where  $J_u$  and  $J_w$  are the fluxes of dissolved solute and soil water, respectively,  $C_u$  is the concentration of dissolved solute,  $D_e$  is the effective diffusion-dispersion coefficient, and  $z$  is vertical coordinate (Jury et al., 1991). In addition to the indications of Biggar and Nielsen (1967) and Bear (1972), Jury et al. (1991) reported that as a simulation model, Eq. (1) suffers from the drawback that its parameters cannot be measured independently in real soils but rather must be curve fitted by simultaneous optimization of all its parameters to outflow data. Also, Biggar and Nielsen (1967) gave the notice that because minute differences in the viscosity and density of the solutions produce measurable changes in the mixing, neither the velocity distribution nor the apparent diffusion (or effective diffusion-dispersion) coefficients will yield a correct description for the cases of solute transport with respect to solution having a wide concentration distribution.

From the above considerations, it is found that the parameters in Eq. (1) can be practically predicted only under the conditions when a velocity distribution as in case of steady flow is already known with assuming that the transition range between two solutions having different concentrations is very narrow, namely, the difference of concentration between solutions is very small. In other words, it should be inadequate to apply Eq. (1) in the solute transport problems with a drastic concentration distribution such as the case that an evaporation boundary condition is established at soil surface, although its initial concentration has a very low and uniform distribution. Under this circumstance, velocity distributions through soil column are largely changed with time, and their changes depend on soil water content and properties. The relatively low velocities during evaporation may produce out the sufficient time and condition that the ratio of molecular diffusion to mechanical dispersion becomes larger than that in higher velocities. Also, the dissolved solute mass in dilute solution is very small in comparison with the related solvent mass, so that both of solute and solvent transport have been exactly detected within an allowed error limit for most practical purposes by using Eq. (1) with the known solution flux. In highly concentrated solution close to saturation, however, the existence of a considerable solute implicates that the change in the solvent part as the counter-part for it in the solute part cannot be neglected. That is, this means the complementary relation between solute and solvent in highly concentrated solution must be considered. Any changes in the properties of the solution due to this relation never overlook. It is doubtful

whether, without considering a simultaneously responsible way to the transient changes of solution properties, the transient analysis of a highly concentrated solution by Eq. (1) can yield a meaningful result equal or close to it in dilute solution, also, in which the soil water flux in Eq. (1) has been often obtained by Darcy's equation without considering the existence of solute in soil solution such as Bresler (1973), Bresler, et al. (1982), etc. Particularly, under the evaporation circumstance, this situation may be occurred at almost all time steps except for a little of duration at initial time step, even if the initial concentration in soil column has a very low and uniform distribution. This concept was given as 'mutual diffusion coefficient' (Sherwood, et al., 1975; Robinson, et al., 1959) and 'interdiffusion coefficient' (Moore, 1972) in describing the diffusion process for binary gas system. The theoretical development for expanding it into binary liquid system and applying to diffusion-dispersion in soil will be discussed in the following report with considering a large description due to its complexness.

We intend to determine the fluxes of solute, solvent, and solution from their profiles obtained by transient evaporation experiment with considering the change of solvent flux as the counterpart for it of a solute flux in solution. The experiment is accomplished by using the ten replica soil columns corresponding with time steps in consideration, in which all soil columns are assumed to have the same pore structure and initial water content and concentration distribution, even if some unevenness exist. Also, the errors due to unevenness are not corrected for preventing an artificial and optional analysis.

## II. Theoretical Considerations

When the mixed solution with a solvent and one or more solutes moves in soil space under transient unsaturated condition, the change of liquid soil water to gaseous soil water (vapor) or dissolved salt to solid one, namely the phase transition can be simultaneously occurred under the corresponding conditions. It is impossible to describe all these phenomena as a single equation. Here, they are divided into some parts for formulating exactly.

### 1. Mass balance

The mass balance equations for solvent water, solute, solution, vapor, air, and mixture gas are given as

$$\text{solvent water} \quad \frac{\partial}{\partial t} c_w \theta + \frac{\partial}{\partial z} f_w = -S_w \quad (2)$$

$$\text{soil solute} \quad \frac{\partial}{\partial t} c_u \theta + \frac{\partial}{\partial z} f_u = -S_u \quad (3)$$

$$\text{soil solution} \quad \frac{\partial}{\partial t} \rho_L \theta + \frac{\partial}{\partial z} f_L = -S_w - S_u \quad (4)$$

$$\text{soil vapor} \quad \frac{\partial}{\partial t} \phi_G c_v + \frac{\partial}{\partial z} f_v = S_w \quad (5)$$

$$\text{soil air} \quad \frac{\partial}{\partial t} \phi_G c_A + \frac{\partial}{\partial z} f_A = 0 \quad (6)$$

$$\text{mixture gas} \quad \frac{\partial}{\partial t} \phi_G \rho_G + \frac{\partial}{\partial z} f_G = S_w \quad (7)$$

respectively, where  $f_w$ ,  $f_u$ ,  $f_L$ ,  $f_v$ ,  $f_A$  and  $f_G$  are mass fluxes of components ( $\text{kg}/\text{m}^2\text{-soil}/\text{s}$ ),  $c_w$ ,  $c_u$ ,  $c_v$  and  $c_A$  are concentrations ( $\text{kg}/\text{m}^3$ ) of components,  $\rho_L$  and  $\rho_G$  are densities of solution and mixture gas,  $\theta$  is volume fraction of soil liquid ( $\text{m}^3\text{-liquid}/\text{m}^3\text{-soil}$ ) and  $\phi_G$  is volume fraction of soil gas ( $\text{m}^3\text{-gas}/\text{m}^3\text{-soil}$ ). And sink/source terms in equations are given as the phase transition rate  $S_w$  that has a positive value in evaporation and

the crystallization rate  $S_u$  that is computed by using the solute concentration and the saturation concentration in soil solution.

## 2. Transport equations

The diffusion process in the binary solution system that is composed of two or more molecules or ions must be described by the mutual diffusion among them (Sherwood, et al., 1975; Robinson, et al., 1959; Moore, 1972). On the contrary, in solute and water transport through soil, since the mutual diffusion is expected to occur at interfaces between different solutions that are produced out by the differences of velocities in soil pores, the mass transport equations for solvent water, soil solute and solution that describe the mutual diffusion-dispersion with convection can be expressed as

$$\text{solvent water} \quad f_w = -\theta D_L \frac{\partial c_w}{\partial z} + c_w \theta U_L \quad (8)$$

$$\text{soil solute} \quad f_u = -\theta D_L \frac{\partial c_u}{\partial z} + c_u \theta U_L \quad (9)$$

$$\text{soil solution} \quad f_L = -\theta D_L \frac{\partial \rho_L}{\partial z} + \rho_L \theta U_L \quad (10)$$

respectively, where  $D_L$  is the apparent mutual diffusion-dispersion coefficient of solution ( $\text{m}^2/\text{s}$ )  $U_L$  and is average flow rate of solution ( $\text{m}/\text{s}$ ).

## 3. Phase transition of soil water

Molar balance for mixture gas with the phase transition is given as the alternative of Eq. (7) for analytical convenience by

$$\frac{\partial}{\partial t} \phi_G \left( \frac{c_v}{M_v} + \frac{c_A}{M_A} \right) + \frac{\partial}{\partial z} \left( \frac{f_v}{M_v} + \frac{f_A}{M_A} \right) = \frac{S_w}{M_v} \quad (11)$$

where  $M_v$  and  $M_A$  are molar masses ( $\text{kg}/\text{mole}$ ). If the pressure of mixture gas  $p$  (Pa) is assumed to

be constant in space and time, the respective components among mixture gas can move but the mixture gas as a whole never move. This means that the second term of Eq. (11) can be neglected. Moreover, if the assumption of ideal gas is valid in soil pores, the relation of

$$\frac{\rho_G}{M_G} = \frac{c_v}{M_v} + \frac{c_A}{M_A} = \frac{P}{RT} \quad (12)$$

can be applied at every space and time in soil, where  $R$  is gas constant ( $\text{J}/\text{K}/\text{mole}$ ),  $T$  is temperature (K) and  $M_G$  is the mean molar mass of mixture gas.

Substituting Eq. (12) into Eq. (11) with no flow assumption for mixture gas and rewriting yields

$$S_w = \frac{M_v P}{RT} \frac{\partial}{\partial t} \phi_G \quad (13)$$

Because in rigid soil the sum of volume fraction of gas and liquid is always constant, the following relation becomes valid.

$$\frac{\partial}{\partial t} \phi_G = -\frac{\partial}{\partial t} \theta \quad (14)$$

By considering the relation with the time derivative of volume fraction of soil liquid, the phase transition rate can be given as

$$S_w = -\frac{M_v P}{RT} \frac{\partial}{\partial t} \theta \quad (15)$$

## 4. Solute crystallization

Establishing a particular condition for evaporation to soil surface, salt deposition can be occurred by phase transition of a part of the dissolved solute in soil solution. Let  $m_u^L$  and  $m_u^s$  be the dissolved solute mass (kg) in solution and the solute mass in solid phase, respectively. Although a part of the solvent water in soil solution is lost by evaporation, the sum of them

$$m_u = m_u^L + m_u^S \quad (16)$$

must remain to be constant. Then we get

$$0 = d(m_u^L) + d(m_u^S) \quad (17)$$

In supersaturation solution, because the difference between dissolved solute mass and solubility  $c_o$  (mass fraction) cannot exist in dissolved state theoretically, we can get the relation as

$$m_u^L = \frac{c_o}{1-c_o} m_w = K_u m_w \quad (18)$$

where  $K_u$  is an inherent value with solute types. By relating Eq. (17) with Eq. (18), the crystallization rate of solute is given as

$$\frac{d}{dt} m_u^S = -\frac{d}{dt} m_u^L = -K_u \frac{d}{dt} m_w \quad (19)$$

That is, this is proportional to the loss rate of water by evaporation. The crystallization rate of solute and the loss rate of water by evaporation, also, have the role of the sink/source terms in mass balance equations. Because of their definitions as

$$S_w = -\frac{1}{V} \frac{\partial}{\partial t} m_w \quad (20)$$

$$S_u = \frac{1}{V} \frac{\partial}{\partial t} m_u^S \quad (21)$$

where  $V$  is soil bulk volume, the relation between  $S_w$  and  $S_u$  is obtained as

$$S_u = \frac{c_o}{1-c_o} m_w = K_u S_w \quad (22)$$

## 5. Getting fluxes from profiles

Eq. (2) to (4) by substituting Eq. (15) are rewritten as

$$\text{solvent water} \quad \frac{\partial}{\partial t} \left[ c_w - \frac{M_v P}{RT} \right] \theta + \frac{\partial}{\partial z} f_w = 0 \quad (23)$$

$$\text{soil solute} \quad \frac{\partial}{\partial t} \left[ c_u - K_u \frac{M_v P}{RT} \right] \theta + \frac{\partial}{\partial z} f_u = 0 \quad (24)$$

$$\text{soil solution} \quad \frac{\partial}{\partial t} \left[ \rho_L - (1+K_u) \frac{M_v P}{RT} \right] \theta + \frac{\partial}{\partial z} f_L = 0 \quad (25)$$

Integrating Eq. (23) to (25) with respect to height  $z$  with the lower end boundary condition  $f|_z=0$  can be obtained by

$$\text{solvent water} \quad f_w = -\frac{\partial}{\partial t} \int_0^z \left[ c_w - \frac{M_v P}{RT} \right] \theta dz \quad (26)$$

$$\text{soil solute} \quad f_u = -\frac{\partial}{\partial t} \int_0^z \left[ c_u - K_u \frac{M_v P}{RT} \right] \theta dz \quad (27)$$

$$\text{soil solution} \quad f_L = -\frac{\partial}{\partial t} \int_0^z \left[ \rho_L - (1+K_u) \frac{M_v P}{RT} \right] \theta dz \quad (28)$$

## III. Materials and Methods

### 1. Materials

Since we intend to determine the fluxes of solute, solvent, and solution from their profiles obtained by transient evaporation experiment with considering the change of solvent flux as the counter-part for it of the solute flux in solution. It is required that any chemical reaction between the solution in soil pores and the components of soil particles is not occurred. The Kujukuri coastal sand was chosen as material that satisfies these requirements. It was taken from the Pacific coast of Chiba, Japan. Its particle density and bulk density are 2.67 and 1.62 Mg/m<sup>3</sup>, respectively. Soil sample was prepared by wash-out, air-drying and 2 mm sieving. Wash-out was continued to use the water of 50 nS/m until the extraction gets to below 100 nS/m. Soil water retentivity curve for pure water is shown in Figure 1. It was determined by gravitational equilibrium, suction plate, pressure plate and vapor equilibrium methods. The saturated hydraulic conductivity was 9.85 × 10<sup>-2</sup> kg s/m<sup>3</sup> by changing head method.

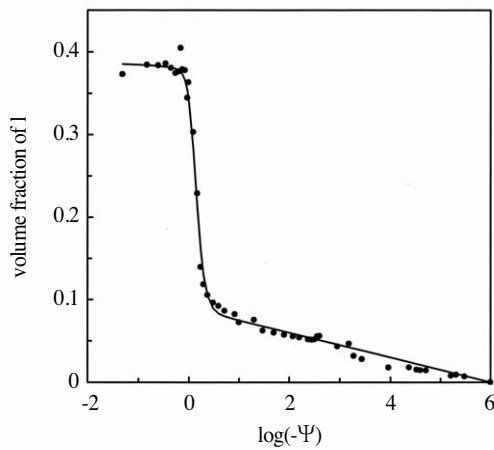


Figure 1. Soil water retentivity for Kujukuri coastal sand.  
Unit of  $\Psi$  is expressed in J/kg

The solution used in experiment was prepared by mixing  $\text{MgCl}_2$  and pure water to be  $22 \text{ kg/m}^3$   $\text{MgCl}_2$  aqueous solution (0.022 in mass fraction). The saturation concentration at  $\text{MgCl}_2$  aqueous solution is known as  $461 \text{ kg/m}^3$  (0.355 in mass fraction). The initial concentration 22 to saturation concentration  $461 \text{ kg/m}^3$   $\text{MgCl}_2$  aqueous solution are converted into the solution densities of 1.019 to  $1.300 \text{ Mg/m}^3$  with a linear relation between solution densities and concentrations in mass fraction.

This experiment prepared ten replica soil columns with an error in order to obtain the transient profiles of various types with respect to solute, solvent, and solution. The errors with initial conditions were examined by the averages, standard deviations, and coefficients of variation of the bulk densities and total solute masses in soil columns. The averages, standard deviations, and coefficients of variation were  $1.623 \text{ Mg/m}^3$ ,  $3.736 \times 10^{-2}$ , and  $2.302 \times 10^{-5}$  in bulk density, and  $1.400 \times 10^{-3} \text{ kg}$ ,  $1.620 \times 10^{-4}$ , and  $1.116 \times 10^{-1}$  in total solute mass, respectively.

## 2. Methods

Soil sample at air-drying was weighed and evenly packed into the column composed of 10 pieces of lucite ring with 49.5 mm in diameter and 10 mm in height. Packing was carried out to weigh the saturated soil column with the initial concentration  $22 \text{ kg/m}^3$   $\text{MgCl}_2$  aqueous solution at every 20 mm in height. The uniformity and accuracy of bulk density in column were checked by the packing test and after experiment, respectively. Evaporation was continued to keep a constant humidity in the plastic box with 225x242x210 mm in inner dimension, where the glass pan with the saturated  $\text{CH}_3\text{COOK}$  aqueous solution of humidity 22.5 % at equilibrium (Greenspan, 1977) and the electrical fan for cycle of inner air were placed below and over soil sample, respectively. Also, the plastic box was set into the chamber with a constant temperature.

The evaporation rates during beginning step from the saturated soil sample surfaces with pure water and  $22 \text{ kg/m}^3$   $\text{MgCl}_2$  aqueous solution were 26.6 and 15.7 mm/day. Samples were drawn out from the plastic boxes at 0, 0.25, 0.67, 1, 2, 4, 8, 12, 19, 30 days, dismantled by blade-cutting, immediately weighed, and dried in the oven that was controlled at 105 degree in Centigrade. After the dried samples were reweighed, they were mixed with the 150ml of pure water in plastic bottles and shaken by vibrator for 1 hour. The solution samples were extracted from them by 0.2 micrometer disc membrane (IWAKI syringe filter 2027-003) for concentration measurement. The ion chromatography device (TOSOH IC-Cation 1/2 HR) was used to decide the concentration of diluted solution sample.

Because it has the measurement range of about 0 to 70 ppm, the solution sample over this range was diluted to adequate concentration. The viscosities of MgCl<sub>2</sub> aqueous solutions with several concentrations were measured by the Ostwald viscometry.

### IV. Results and Discussions

The performances on transient transport of soil solute and solvent water by the evaporation experiment under a constant humidity and temperature are shown as various types of profiles. The volume fraction profiles of soil solution and solvent water are given in Figure 2, where the solid and broken lines indicate the calculated profiles for soil solution and solvent water, respectively. The latter means a virtual volume fraction in solution and is defined by

$$\theta_w = \theta_L \frac{\rho_L - c_u}{\rho_w} \tag{29}$$

where  $\rho_w$  is density of pure water. Both are almost the same at high content, but the slight discrepancies are occurred at low content. The

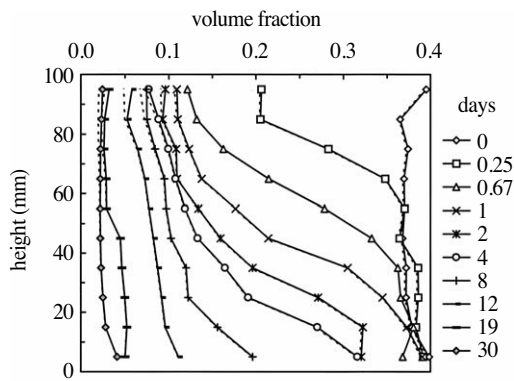


Figure 2. Volume fraction profiles for solution (solid) and solvent (broken).

profiles obtained using the pure water under the same conditions show the similar trend with those for soil solution in that the contents of soil solution gradually decreased from sample bottom. During the late time steps, it should be noted that the volume fractions of solution near sample surface is higher than those at lower layers.

Figure 3 shows the profiles of solute content in soil solution and their unit, kg-solute/kg-solid soil means the total solute content in bulk soil solution. A part of soil solute is crystallized near sample surface during the late time steps. Assuming that the saturation concentration in soil solution is the same as it in free solution, we can divide the solute mass in solution and crystal from the soil solution with the excess solute concentration over the saturation concentration. At the profiles of 12, 19 and 30 days, the values of 90-100 mm layer are obtained by the elimination of crystallized solute part from supersaturation solution.

The soil solute having even distribution at the beginning time moves upward to soil sample surface as time advances. As the result, the content of soil solute decreases in the lower layers of soil

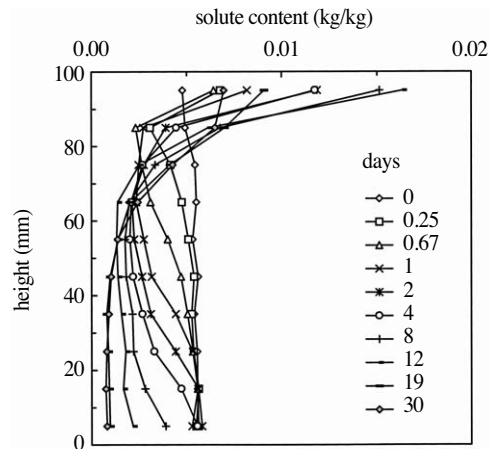


Figure 3. Profiles of soil solute content

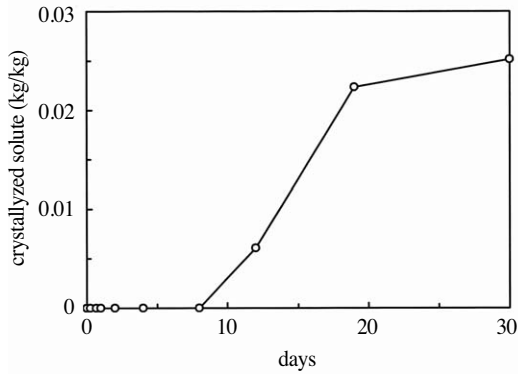


Figure 4. Change of cumulative crystallized solute production with time

sample with increasing near its surface. Figure 4 shows the cumulative production of crystallized solute in the 90-100 mm layer with time. The crystallization is first occurred at 8 days and at the final time it attains to the 50.2% of total solute that existed to be dissolved at the beginning. By subtracting the part of crystallized solute in soil solution, the profiles for solvent water and solvent concentration and solution density are shown as in Figures 5, 6 and 7, respectively. Solvent water concentrations indicate the tendency that is slight-

ly decreased near the sample surface, this situation should be caused by solute accumulation near sample surface (Figure 5). While the solute concentration profiles have the larger changes than the cases of solvent water, especially these situations are significantly shown near sample surface (Figure 6). Also, the solution density profiles in Figure 7 are given as the results that Figures 5 and 6 are reflected together.

The mass fluxes for solvent water and solute that are obtained from Eqs. (26) and (28), are shown in Figures 8 and 9, respectively. Solvent water fluxes largely increase in the upper layers of 0.25 and 0.67 days, after 1 day their profiles go to gradually decrease with a similar type (Figure 8). The cases of solute fluxes also show the similar trends as those of solvent water fluxes, but their slopes are converted to be negative near sample surface except for 12 and 19 days (Figure 9). The conversion of slopes should manifest the predomination of downward diffusion by the solute accumulation near sample surface. The exceptional values at sample surface of 12 and 19

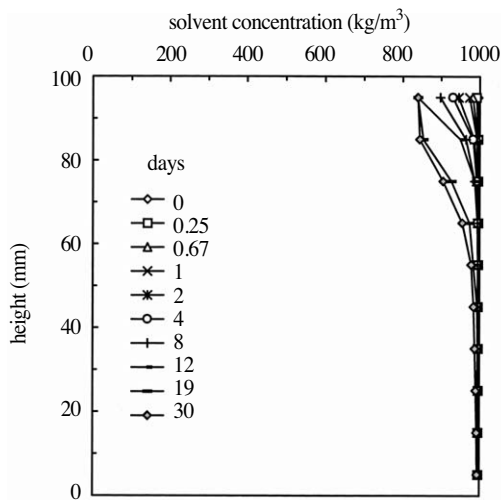


Figure 5. Profiles of solvent water concentration

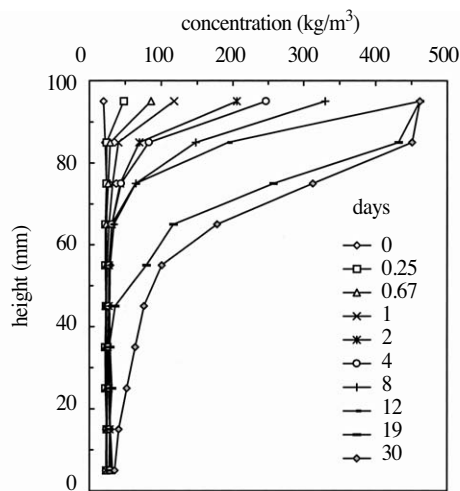


Figure 6. Profiles of solute concentration



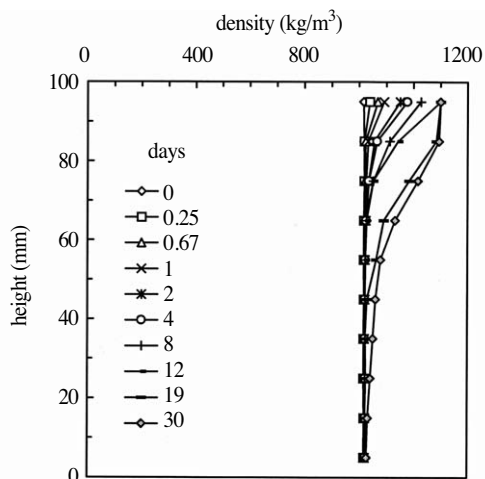


Figure 7. Profiles of solution density

days should be regarded whether to be arose from the lack of knowledge at present about the relation between solution concentration and solution density in soil solution or to be occurred by an error of experiment. Also, because of no migration of solute through the upper boundary and no flow at the lower one, the flux at each time step must be converged to zero, but the

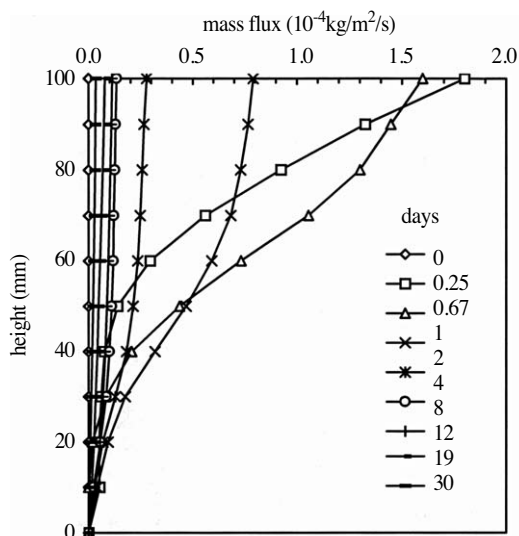


Figure 8. Mass flux profiles of solvent water

fluxes in Figure 9, particularly at 0.25 and 0.67 day are deviated from it. They are thought to be caused by uneven initial total solute masses in soil columns with the coefficient of variation 0.1157. However, we didn't correct the errors due to the differences in initial solute mass for preventing artificial and optional analysis.

Figure 10 shows that the solvent fluxes have a good correlation with the solution fluxes ( $R^2=1$ , in which  $R^2$  is coefficient of determination). On the contrary, the relation between solute and solution shows to be slightly scattered with  $R^2=0.8821$  (Figure 11). Comparing the solute fluxes in Figure 11 with the solvent fluxes in Figure 10, the former values are extremely less than the latter. From these results, it is found that almost all solvent and solute are transported as solution together (this is called 'convection'), and only a slight part of solute migrates a different manner with it in solution (this has been called 'diffusion-dispersion' or 'hydrodynamic dispersion', but it is defined as 'mutual diffusion-dispersion' in this

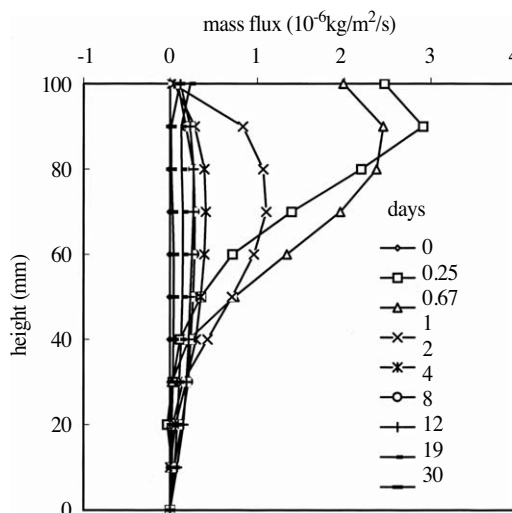


Figure 9. Mass flux profiles of soil solute

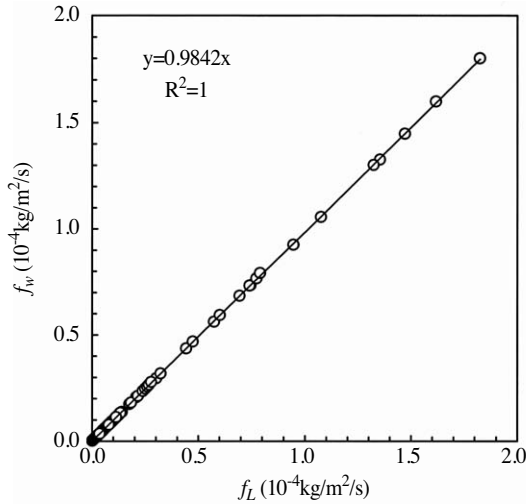


Figure 10. Correlation between solvent and solution flux

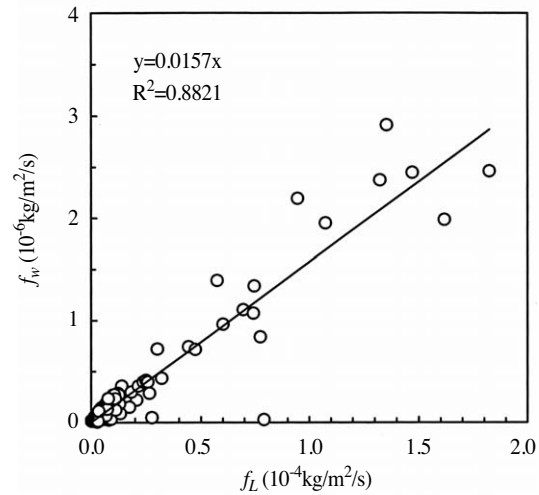


Figure 11. Correlation between solute and solution flux

paper). Then, in the research of the solute and water movement through porous media, it is a most important subject to manifest the behavior of solution not only in low concentrated solution but also in highly concentrated one. However, it should be noted that no doubt there are considerable changes in the properties of solution with the increases of solute concentration. Biggar and Nielsen (1967) indicated that minute differences in viscosity and density of the solution produce measurable changes in mixing, and a most responsible cause for this changes should be the effect of solute concentration on behavior of solution. The behavior of solution through soil has been often considered by Darcy's equation without considering the existence of solute in soil solution such as Bresler (1973), Bresler et al. (1982), etc, although Low (1955) and Kemper and Evans (1963) tried to describe the effect of solute concentration on Darcy's equation without a clear theoretical basis and sufficient information. Therefore, we could take much knowledge about

the effect of solute concentration on behavior of solution from the fluxes of solute, solvent, and solution obtained in this paper.

In order to examine the above fluxes in detail, the mass concentration gradients for solvent and solute are shown in Figures 12 and 13. Both have similarly large changes near sample surface, but their signs are opposite. If the solute or solvent transport in soil pores is caused by the concentration gradient, therefore, the flow directions of them should have to be opposite, also.

As shown before, all the calculated fluxes in Figures 8 and 9 have positive values. This means they flow upward as a whole. Supposing that the existence of certain downward flows is admitted by the concentration gradients in Figures 12 and 13, the relations among the components of fluxes may be comprehensively shown as Figure 14, in which numerals are the average values. The relation among the components of solution fluxes is, in detail, described at later. At present, therefore, it is difficult to define the convection terms in

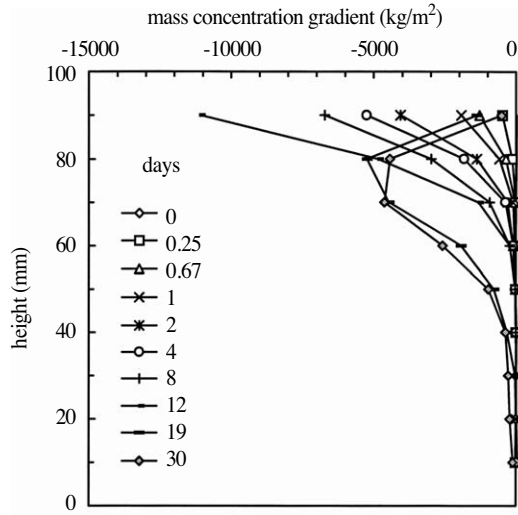


Figure 12. Mass concentration gradient profiles for solvent water

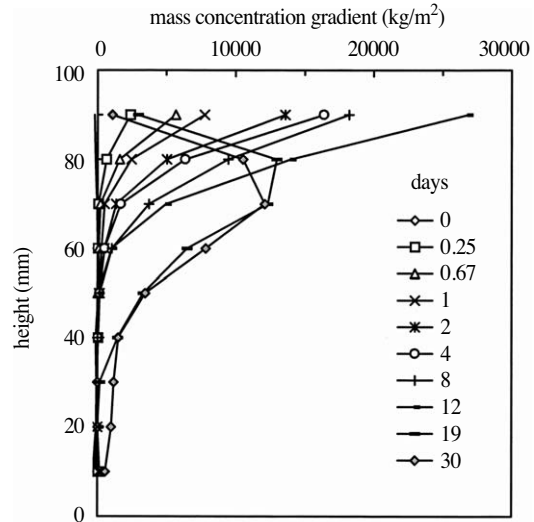


Figure 13. Mass concentration gradient profiles for soil solute

Eqs. (8) to (10) as a particular expression that can be autonomously determined. From the experiment results of this study, however, it is possible to confirm the magnitude of fluxes by using mass balance as the following.

Since all the measured fluxes are divided into the mutual diffusion-dispersion and convection parts, in which the respective parts are not clearly separated but their nomenclatures are given by terminological convenience, Eq. (8) and (9) can be rewritten as

$$\text{solvent water } f_w = f_{w1} + f_{w2} \tag{30}$$

$$\text{soil solute } f_u = f_{u1} + f_{u2} \tag{31}$$

where the 1 and 2 in subscripts indicate the mutual diffusion-dispersion and convection flows, respectively. Let the mutual diffusion-dispersion flux  $f_{u1}$  and convection flux  $f_{u2}$  have the relations as

$$f_{u1} = af_{w1} \tag{32}$$

$$f_{u2} = bf_{w2} \tag{33}$$

respectively, where  $a$  and  $b$  are given as

$$a = \frac{\partial c_u / \partial z}{\partial c_w / \partial z} \tag{34}$$

$$b = \frac{c_u}{c_w} \tag{35}$$

Since the values of  $a$  and  $b$  can be obtained from the measured data, we can have the solute flux with respect to the solvent terms as

$$f_u = af_{w1} + bf_{w2} \tag{36}$$

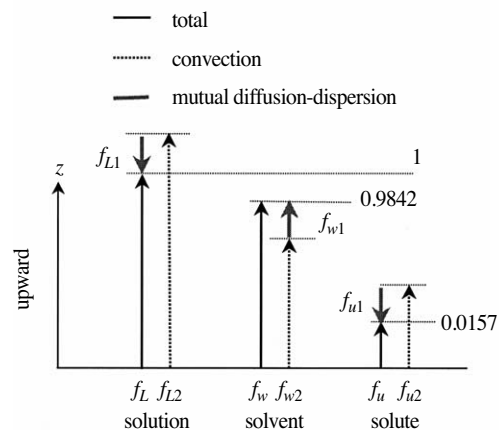


Figure 14. Schematic comparison of fluxes in binary solution system of soil

From Eqs. (30) and (36), we can determine the components of flux as

$$f_{w1} = \frac{f_u - bf_w}{a - b} \tag{37}$$

$$f_{w2} = -\frac{f_u - af_w}{a - b} \tag{38}$$

The components of soil solute flux are also given by Eqs. (37) and (38) into Eqs. (32) and (34).

The components of fluxes for solvent water and soil solute estimated by using Eqs. (30) to (38) are shown in Figures 15, 16, 17, and 18, respectively. The convection fluxes for solvent water have extremely higher order of magnitude and different shape than others. From these mutual diffusion-dispersion and convection fluxes, we can determine the “mutual diffusion-dispersion coefficients” and the flow rates of solution. The mean value of the former over all processes is  $9.8 \times 10^{-9} \text{ m}^2/\text{s}$  and does not have a particular relation with the flow rate. Robinson and Stokes (1959) tabulated the diffusivity of  $\text{MgCl}_2$  as  $1.187 \times 10^{-9} \text{ m}^2/\text{s}$  in dilute of concentra-

tion  $0.0952 \text{ kg/m}^3$  (0.001 mole/l) at 25 degree in Centigrade. Solution diffusivity is inversely proportional to viscosity  $\mu$  by Stokes-Einstein so that

$$D/D_0 = \mu_0/\mu \tag{39}$$

where subscript 0 means the appropriate state. Accordingly, the diffusivity in free solution at saturation is computed as  $1.49 \times 10^{-10} \text{ m}^2/\text{s}$ . Comparing the diffusivity in free solution  $1.49 \times 10^{-10} \text{ m}^2/\text{s}$  with the mutual diffusion-dispersion coefficient  $9.8 \times 10^{-9} \text{ m}^2/\text{s}$  in this analysis, the former is about one order smaller than the latter. This difference should be caused by mutual diffusion-dispersion that has the meaning of the mutual diffusion of solute and solvent in the interfaces between the solutions of their different concentrations, in which these interfaces are mainly formed by mechanical dispersion that considers the differences of velocities in soil pores. And it perhaps is different from the case of break through curve experiments. Olsen and Kemper (1968) calculated the diffusion-dispersion

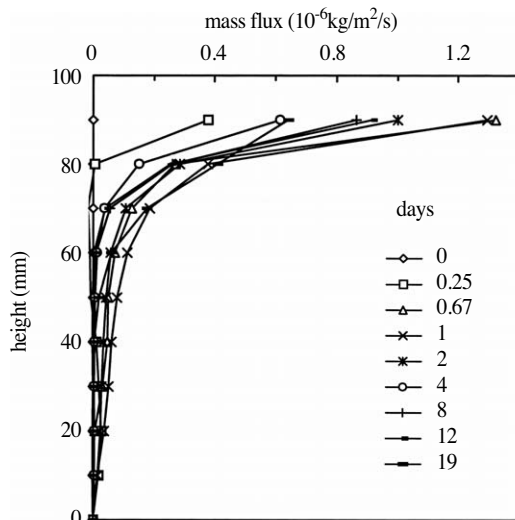


Figure 15. Mutual diffusion-dispersion flux profiles for solvent water

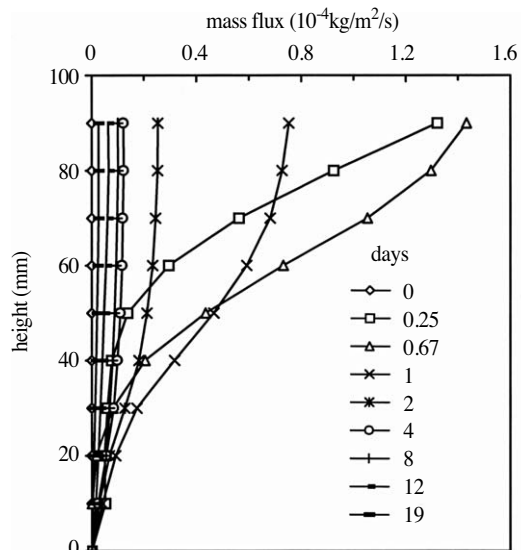


Figure 16. Convection flux profiles for solvent water

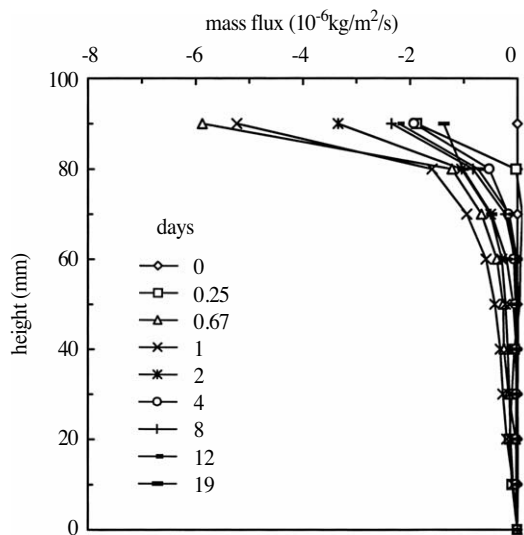


Figure 17. Mutual diffusion-dispersion flux profiles for soil solute

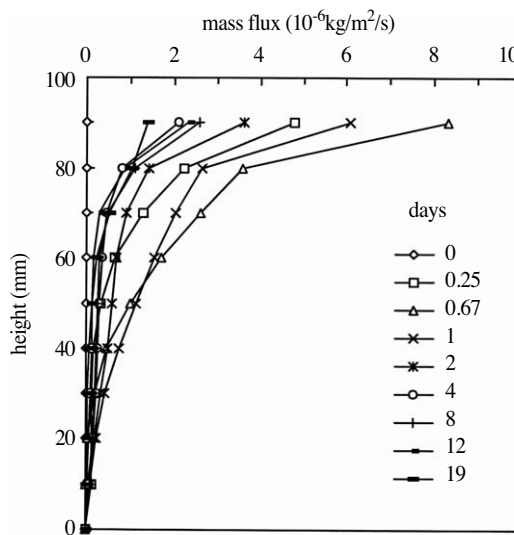


Figure 18. Convection flux profiles for soil solute

coefficient from the data of Nielsen and Bigger (1962, 1963) and reported its dependence on the flow rate. Also, Nye and Tinker (1977) insisted its validity by quoting a similar result after Pfannkuch (1963). These results were almost obtained from the situations that as in break through curve experiment, diffusion-dispersion and convection fluxes are conducted toward the same direction, but in this study, the mutual diffusion-dispersion flux have the opposite direction against the convective fluxes. Therefore, it is not surprising that the independence of the mutual diffusion-dispersion coefficient on the flow rate of solution is obtained as a result in this analysis, even if it is different with past works.

The mutual diffusion-dispersion fluxes for solution in Figure 19 must agree with the sum of them for solvent and solute. All fluxes have negative values so that the solution transport by the effect of mutual diffusion-dispersion is directed downward, while the mass gradients for solution

have positive values. Therefore, as shown in Figure 14, the convection fluxes for solution should have larger values than those measured.

Finally, we compare total solute mass fluxes with convection fluxes in Figure 20. From the conformity of profiles in the lower parts of sam-

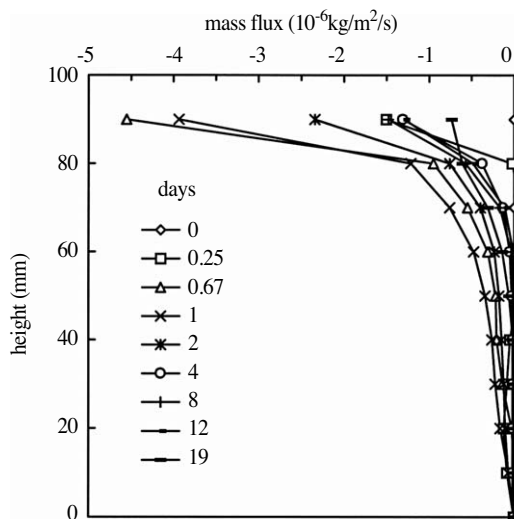


Figure 19. Mutual diffusion-dispersion flux profiles for soil solution

ple, it is clarified that most of solute fluxes are occurred by convection fluxes. Also, the discrepancy of profiles in the upper parts of sample indicates that the predominance of mutual diffusion-dispersion in relation with the other places in soil columns.

## V. Conclusion

Environmental impact assessment requires the procedure for predicting the responses obtained by adding some expectable changes of conditions or parameters to a specified environmental system, in which this system is inherently the complex that is composed by the parameters having some mutual relationships between them. It could be necessary to produce out the governing equation that the mutual relationships between parameters are sufficiently considered.

Mass balance equations for simultaneous transport of solvent and solute through soil are formulated with the consideration of phase transition rate. This study pointed out that if the soil solute transport is subjected by the mutual diffusion-dispersion with convection, the complementary relation between solute and solvent in solution should be introduced into binary system of soil solution. By defining heteronomous equations for considering this relation, the fluxes of solute, solvent, and solution are determined from the evaporation experiment of this paper, and their details are manifested. The results are as follows.

It is no doubt that most of solute are transported by convection not only in low concentrated solution but also in high one, and only a slight solute are migrated by mutual diffusion-dispersion. But, it should be noted that a considerable

solute are contained in highly concentrated solution. Considering the complementary relation between solute and solvent in solution, a slight change of solute mass in solution might produce out larger change ratio in solute concentration than it in solute mass. Also, it is a problem prior to the others to obtain the adequate transport equation for simultaneously treating the behavior of solution with the changes of solute concentration in transient analysis. Any proportional relation between mutual diffusion-dispersion coefficients and the flow rates of solution cannot be defined as the past works, even if they have high correlation. It is confirmed that the mutual diffusion-dispersion fluxes for solution direct downward with the same values as the sums of solute and solvent by the solution density gradients. In addition, it is recommended to investigate the relation between total and mutual diffusion-dispersion fluxes in solute transport in detail.

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