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NUMERICAL SIMULATION FOR TRANSPORT OF CHLORINATED HYDROCARBONS WITH GAS ADVECTION AND DIFFUSION IN UNSATURATED ZONE

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SYNOPSIS

Chlorinated hydrocarbons(CHC) are volatile substances and they exist in unsaturated zone, as dissolved, gaseous and dense non-aqueous phases. Recently, a vacuum extraction method has been enlisted as one of the best recovery methods against contaminated soil. To make effective *in situ* remediation by this method, it is indispensable to understand mechanism of CHC transport concerning advection, diffusion and volatilization in unsaturated and saturated zones. This paper examined transport mechanisms of volatilized and dissolved CHC from dense non-aqueous phase liquid(DNAPL) in unsaturated zone by numerical analysis. In our numerical model, cylindrical fluid flow and mass transport equations for water and gas phases, and the two layer model for mass transfer between the phases were developed. As a result, it was clarified that gas transport and mass transfer process between water and gas phases play an important role in existence of CHC in unsaturated zone where groundwater flow does not take place.

INTRODUCTION

At present, the following methods are considered as recovering countermeasures against soil and groundwater contaminations by chlorinated hydrocarbons(CHC),

1. Pumping up contaminated groundwater from wells: This method is the most common as recovering countermeasure of contaminated groundwater and is effective to remove CHC from aquifer and to prevent CHC from spreading to downstream. (Freeberg et al.,(3))
2. Vacuuming CHC gas in unsaturated zone (vacuum extraction method): This method is effective to remove CHC in unsaturated zone and to prevent CHC from infiltrating into deeper aquifer. (Urlings et al.,(11))
3. Biodegradating CHC into harmless substance: To apply this method, it is important to examine influence of microbes or byproducts. At present, many researches to discover effective microbes or byproducts are being carried out. (Yagi and Uchiyama,(13))

Among these methods, the second method is considered to be the most effective countermeasure against soil and groundwater contaminated by CHC. And this method has been carried out in many fields. In practice, however, it has been also reported that CHC concentration in groundwater or soil gas increased after pumping up contaminated groundwater and vacuuming CHC gas in some fields(Tajima et al.,(10)). This may suggest that an accurate evaluation of behavior of CHC gas in unsaturated zone and adoption of efficient countermeasures were necessary. Sleep and Sykes(9) discussed the importance of gas phase transport and mass transfer between the phases in unsaturated zone. Mendoza and McAlary(5) verified that, in highly permeable zone, density-driven advection of soil gas played an important role. The authors also analyzed various mechanisms of CHC transport with gas diffusion in unsaturated zone and mass transfer process between water and gas phases by numerical model and one dimensional column experiments(Egusa et al. (2)). In this paper, we attempted to clarify transport mechanism of volatilized and dissolved CHC from dense non-aqueous phase liquid (DNAPL) in unsaturated zone where groundwater flow hardly took place by numerical analysis.

BASIC EQUATIONS FOR THE NUMERICAL ANALYSIS

There should be two possible routes of infiltration of CHC into aquifer. One is the infiltration of dissolved CHC from natural river bed or drainage channel, the other is that of DNAPL from storage tanks. In the former case, CHC exists as dissolved and gaseous phases in water and pore space, while in the latter case, CHC also exists as dissolved, gaseous and non-aqueous phase in aquifer. Since DNAPL breaks into small pieces and percolates randomly while infiltrating into aquifer, it may not be easy to simulate such movement of DNAPL. However, the movement of DNAPL with groundwater flow is negligible. Therefore, we assume that DNAPL will not move when DNAPL in unsaturated zone is regarded as source of contamination.

In our numerical study, the cylindrical fluid flow and mass transport equations of CHC in water and gas phases and the two layer model(Sleep and Sykes (9), Vilker and Parnas (12)) for mass transfer between the phases were applied. In the two layer model, it was assumed that the driving forces of mass transfer is proportional to the differences between the equilibrium and actual concentration on the interface.

1. Water flow equation

$$C_{Lg}\frac{\partial h_g}{\partial t}+C_{LL}\frac{\partial h_L}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left[r k_L\frac{\partial h_L}{\partial r}\right]+\frac{\partial}{\partial z}\left[k_L\left(\frac{\partial h_L}{\partial z}+1\right)\right] \tag{1}$$

2. Gas flow equation

$$\theta_g\frac{\partial \rho_g}{\partial t}+\rho_g C_{gg}\frac{\partial h_g}{\partial t}+\rho_g C_{gL}\frac{\partial h_L}{\partial t}=\frac{1}{r}\frac{\partial}{\partial r}\left[r k_g\rho_g\frac{\partial h_g}{\partial r}\right]+\frac{\partial}{\partial z}\left[k_g\rho_g\left(\frac{\partial h_g}{\partial z}+\frac{\rho_g}{\rho_L}\right)\right]$$
$$+\theta_g\lambda_H(H\cdot C_L-C_g)+\theta_g\lambda_V(C_{gmax}-C_g) \tag{2}$$

3. Transport equation for dissolved CHC

$$R_L\frac{\partial(\theta_L C_L)}{\partial t}+u_L'\frac{\partial(\theta_L C_L)}{\partial r}+v_L'\frac{\partial(\theta_L C_L)}{\partial z}=\frac{1}{r}\frac{\partial}{\partial r}\left[r\theta_L D_{Lrr}\frac{\partial C_L}{\partial r}+r\theta_L D_{Lrz}\frac{\partial C_L}{\partial z}\right]$$
$$+\frac{\partial}{\partial z}\left[\theta_L D_{Lzr}\frac{\partial C_L}{\partial r}+\theta_L D_{Lzz}\frac{\partial C_L}{\partial z}\right]+\theta_g\lambda_H(C_g-H\cdot C_L)+\theta_L\lambda_D(C_{Lmax}-C_L) \tag{3}$$

4. Transport equation for volatilized CHC

$$R_g\frac{\partial(\theta_g C_g)}{\partial t}+u_g'\frac{\partial(\theta_g C_g)}{\partial r}+v_g'\frac{\partial(\theta_g C_g)}{\partial z}=\frac{1}{r}\frac{\partial}{\partial r}\left[r\theta_g D_{grr}\frac{\partial C_g}{\partial r}+r\theta_g D_{grz}\frac{\partial C_g}{\partial z}\right]$$
$$+\frac{\partial}{\partial z}\left[\theta_g D_{gzr}\frac{\partial C_g}{\partial r}+\theta_g D_{gzz}\frac{\partial C_g}{\partial z}\right]+\theta_g\lambda_H(H\cdot C_L-C_g)+\theta_g\lambda_V(C_{gmax}-C_g) \tag{4}$$

where subscripts L and g represent water and gas phases, respectively; C_{Lg} ($=\partial\theta_L/\partial h_g$), C_{LL}($=\partial\theta_L/\partial h_L$), C_{gg}($=\partial\theta_g/\partial h_g$) and C_{gL}($=\partial\theta_g/\partial h_L$) = specific moisture capacities between different phases(Parker et al. (7)); r and z = coordinates in cylindrical and vertical directions; k_L and k_g = hydraulic conductivities; h_L and h_g = pressure heads; C_L and C_g = CHC concentrations; C_{Lmax} and C_{gmax} = saturated concentrations; u_L', u_g', v_L' and v_g' = pore velocity components; D_L and D_g = tensors of dispersivity; ρ_L and ρ_g = densities; θ_L and θ_g = water and air contents; R_L and R_g = retardation factors; H = Henry constant; λ_H = mass transfer coefficient between water and gas phases; λ_D and λ_V = rates of dissolution and volatilization from DNAPL. Besides the above equations, relationship between soil water content and capillary force ($h_{gL}=h_g-h_L$) given by Parker et al.(7) was applied.

The third terms on the right hand side in Eqs. 2, 3 and 4 express the exchange rate of mass transfer between water and gas phases. If actual gas concentration (C_g) is smaller than equilibrium concentration in gas phase expressed by Henry's law as $C_H=H\cdot C_L$, then volatilization of CHC gas from water phase takes place, while dissolution of CHC gas takes place if $C_g > C_H$. The fourth terms on the right hand side in Eqs. 2, 3 and 4 represent volatilization or dissolution rates from DNAPL to gas or water phase.

NUMERICAL SIMULATION

Figure 1 shows the contour lines of Tetrachloroethylene (PCE) gas concentration measured by a detector tube at the depth of 80 cm in laundry yard. Contour lines of PCE gas indicate an evidence of concentric spread from pollutant source. In many sites where groundwater is contaminated by CHC, it is similarly observed that CHC gas spread concentrically from the sources. Groundwater table was observed at the depth of about 2 m, and the unsaturated zone was formed in weathered granite (Egusa et al. (1)). The points of A and B were used to be sludge yard, and plenty of DNAPL was discovered in unsaturated zone at the point of A. In this study, we considered that the point of A was pollutant source (see Figure 1). Simulation area in cylindrical model is shown in Figure 2.

Iterated Alternative Direction Implicit Method(IADI)(Kinzelbach (6)), which is one of finite difference methods, was employed for water and gas flow equations (Eqs. 1 and 2). Method of Characteristics(MOC)(Pinder and Cooper (8), Jinno and Ueda (4)) was used for water and gas transport equations (Eqs. 3 and 4). Boundary conditions of Eqs. 1 through 4 are shown in Figure 2. Impermeable conditions for Eqs. 2 and 4 were given as upper boundaries, because ground surface has been

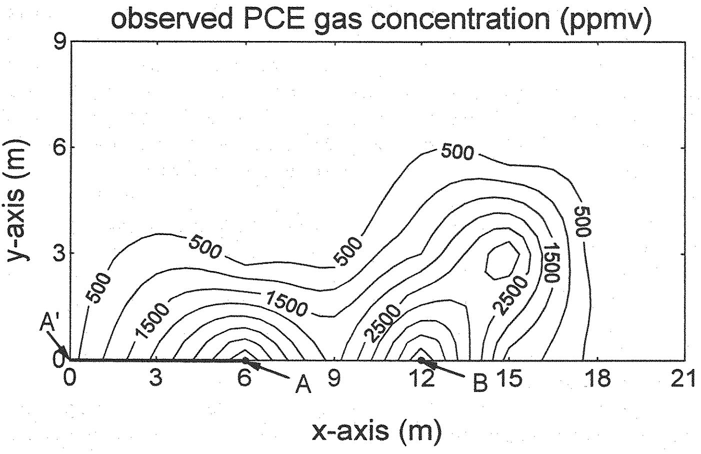

Fig.1 Contour lines of observed concentration of PCE gas at the depth of 80 cm.

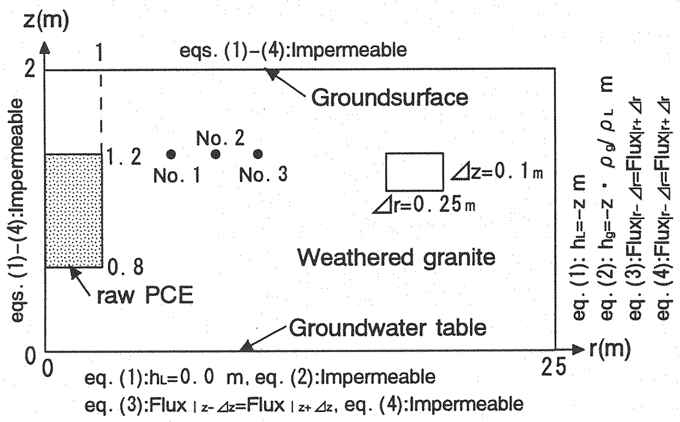

Fig.2 Simulation area

Table.1 Simulation parameters

Parameter	Value
Saturated hydraulic conductivity of water (m/sec)	5.2×10^{-5}
Saturated hydraulic conductivity of gas (m/sec)	3.7×10^{-6}
Saturated water content (Porosity): θ_s	0.45
Residual water content: θ_r	0.15
Longitudinal dispersivity: α_L (m)	0.01
Transverse dispersivity: α_T (m)	0.001
Molecular diffusion coefficient in water: D_L^* (m^2/sec)	1.515×10^{-9}
Molecular diffusion coefficient in gas: D_g^* (m^2/sec)	1.0×10^{-5}
Tortuosity: τ	0.66
Retardation factor: R_L , R_g	1.0
Henry constant: H	1.2
Mass transfer coefficient: λ_H , λ_D , λ_V (1/sec)	2.0×10^{-6}
Saturated PCE concentration in water: C_{Lmax} (kg/m^3)	0.15
Saturated PCE gas concentration in gas: C_{gmax} (kg/m^3)	0.18

covered with concrete floor until laundry was closed. It was assumed that DNAPL of about 7 kg existed at the depth from 0.8 m down to 1.2 m in range of r=0 m to 1 m. Parameters used for this simulation are listed in Table 1. In the two layer model, mass transfer coefficients are very important. Sleep and Sykes(9) suggested that mass transfer coefficients range from 0.1/day (1.14×10^{-6}/sec) to 0.5/day(5.79×10^{-6}/sec). In this case, 2.0×10^{-6}/sec was employed. This value was obtained by one-dimensional column experiments and numerical simulation (Egusa et al. (2)).

Figure 3 shows flow patterns of soil gas, contour lines of dissolved and volatilized PCE after 10, 35 and 50 days in this simulation. DNAPL has disappeared after 34.45 days. In early stage (within 10 days), concentration of dissolved PCE is higher than that of PCE gas near pollutant source. However, gas concentration is higher than dissolved PCE around pollutant source. Molecular diffusion coefficient in gas phase is much larger than that in water phase. And soil gas velocity increases due to volatilization of DNAPL and steep gradient of soil gas pressure in this field. As a result, since gas transport with advection and diffusion is dominant than that of dissolved PCE in unsaturated zone where soil water flow hardly takes place, gas concentration is higher than dissolved PCE around pollutant source.

Gas flow from the pollutant source may take place both in the directions of ground surface and groundwater table. However, soil gas does not flow out from

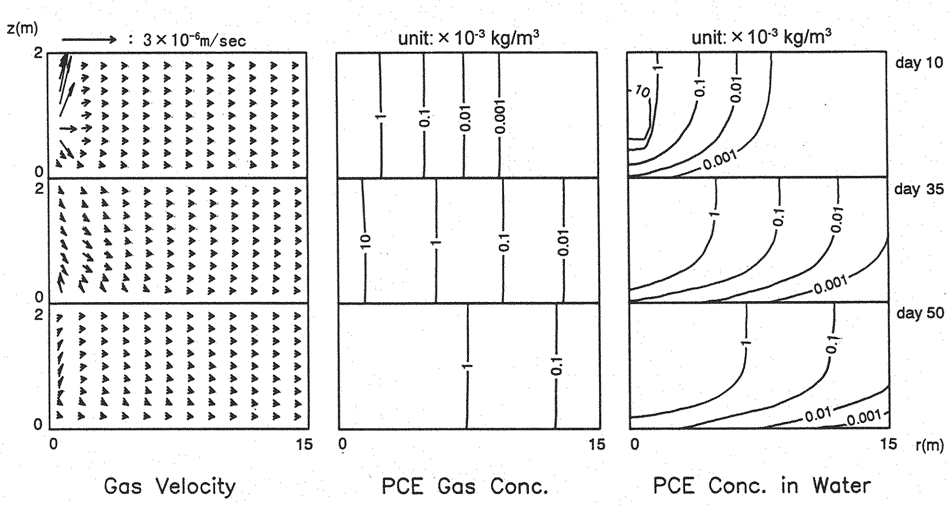

Fig.3 Flow patterns of soil gas, contour lines of volatilized and dissolved PCE (top:10days, middle:35days, bottom:50days).

ground surface, because ground surface is an impermeable boundary in this simulation. Similarly, an impermeable boundary condition is given on groundwater table. As a result, gas concentration spread uniformly in vertical direction at the site where unsaturated zone is narrow and upper boundary is impermeable. On the other hand, dissolved concentration near groundwater table could not increase. This is due to that dissolution rate of PCE gas decreased there, since air volume was small due to capillary water rise and consequently the transport of PCE gas toward groundwater table hardly occurred.

It was observed that vertical flow to groundwater table becomes dominant after 35 days. This is due to that effect of gravitational force of volatilized PCE, so-called density flow, becomes more dominant as gas concentration increases near the pollutant source. Concentration near the pollutant source after 50 days becomes lower than that of after 35 days, because supply of PCE becomes zero.

Figure 4 shows the time series of PCE gas concentration(C_g), dissolved concentration(C_L) and equilibrium concentration between water and gas phases($H \cdot C_L$) at the points of No.1(r=3m), No.2(r=6m) and No.3(r=9m). Gas concentration is higher than equilibrium concentration and consequently PCE gas dissolves into soil water. This fact shows that the spread of PCE through water phase depends on dissolution of PCE gas, since the transport in water phase is much less than that in gas phase when soil water flow hardly occurs. At the point No.1 the near pollutant source, gas concentration quickly increases with gas transport due to volatilization from DNAPL. After DNAPL disappears and supply of gas stops, gas concentration decreases more than that of dissolved PCE, since gas transport with advection and diffusion is still large. As a result, gas concentration at this point becomes lower than equilibrium concentration determined by Henry's law, and consequently PCE begins to volatile through interface between water and gas phases. Simultaneously, the decrease rate of gas concentration gradually becomes small. This will be explained that gas transport decreases there, since advection and diffusion of PCE gas also becomes smaller as total gas pressure and gradient of gas concentration decreases after supply of PCE gas ceases. At the final stage, gas concentration reaches equilibrium concentration of Henry's law. Volatilization through interface between water and gas phases ceases at this stage. Similar behaviors are observed at the points of No.2 and No.3 although these points are located further from the source.

Figure 5 shows calculated and observed profiles of PCE gas along A-A'

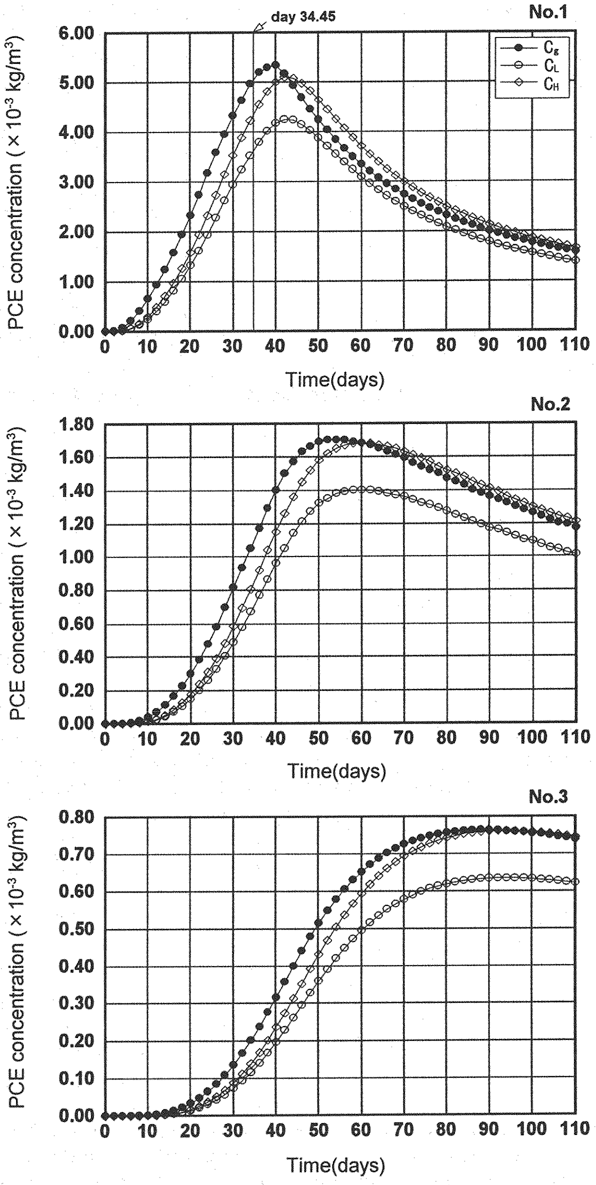

Fig.4 Time series plots of PCE gas concentration (C_g), dissolved concentration (C_L) and equilibrium concentration between water and gas phases ($C_H=H\cdot C_L$) at the points of No.1, No.2 and No.3.

transection Figure 1 with distance from the source at the depth of 80 cm. It is hard to compare calculated concentration with observed one quantitatively , because we do not know duration of contamination and total amount of DNAPL which infiltrated in this field. Therefore, concentrations normalized by the maximum value of each time step are drawn at each time. Profiles of calculated concentrations after 10, 20 and 30 days are almost consistent with observed profiles. Because DNAPL was discovered at the point A when field survey was carried out, transport mechanisms simulated in this study would take place in this field while DNAPL exits in unsaturated soil. Accordingly, observed profiles should be still at stage of volatilization from DNAPL and gas concentration tends to increase due to volatilization. In this simulation, it is shown that the gradient of gas concentration becomes small after DNAPL disappears.

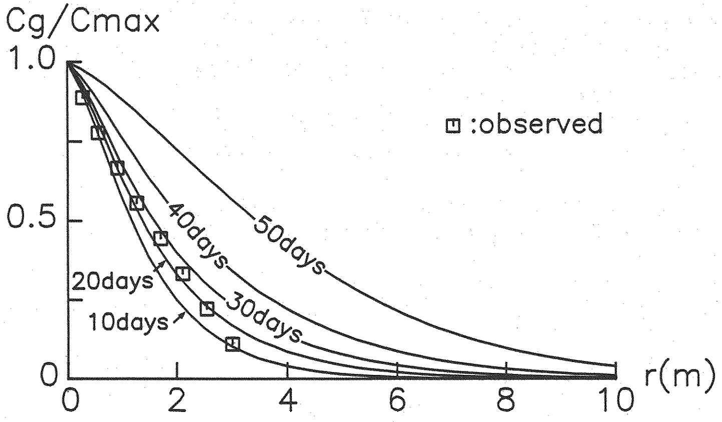

Fig.5 Calculated and observed profiles of PCE gas along A-A' line in Fig.1 with distance from source at 80 cm depth.

CONCLUSIONS

In this study, the transport mechanisms of volatilized and dissolved PCE from DNAPL in unsaturated zone have been examined by numerical simulation . As a result, it is clarified that gas transport is much dominant than that of dissolved PCE in unsaturated zone where groundwater flow hardly takes place, and therefore spread of PCE through water phase depends on that of PCE gas. In our previous study, however, it was obtained that transport of dissolved TCE is dominant than that of TCE gas and the existence of TCE in gas phase depends on dissolved TCE in highly permeable unsaturated and saturated zones(Egusa et al.,(2)).

PCE gas concentration spreads uniformly in vertical direction at the site where unsaturated zone is narrow and upper boundary is impermeable. Material permeability in this field is 6.08×10^{-13} m^2. Mendoza and McAlary(5) discussed that gas transport due to molecular diffusion is dominant in CHC transport processes in unsaturated zone where material permeability is not so high(=8×10^{-12} m^2). The profiles in this study does not differ so much from their simulation result. However, they also discussed that density-driven advection of soil gas plays an important role in highly permeable zone(=8×10^{-11} m^2).

These facts show that it is necessary to take into consideration field conditions of contamination and soil properties to analyze and evaluate transport mechanisms of CHC in unsaturated and saturated zones.

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APPENDIX - NOTATION

The following symbols are used in this paper:

C_{Lg} , C_{LL} , C_{gg} , C_{gL} = specific moisture capacities;

r, z = coordinates in cylindrical and vertical directions;

k_L , k_g = hydraulic conductivities;

h_L , h_g = pressure heads of the phases;

C_L , C_g = CHC concentrations;

C_{Lmax} , C_{gmax} = saturated concentrations;

u_L', u_g', v_L', v_g' = actual velocity components;

D_L , D_g with subscripts = tensors of the dispersivities;

ρ_L , ρ_g = densities;

θ_L , θ_g = water and air contents;

R_L , R_g = retardation factors;

H = Henry constant;

λ_H = mass transfer coefficient between water and gas phases;

λ_D , λ_V = rates of dissolution and volatilization from DNAPL.

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