

(11) Evaluation for the behavior of LNAPL released in vadose zone as source of groundwater contamination

不飽和帯に漏洩された LNAPL 汚染源動態の評価

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**ABSTRACT;** Behavior of light non-aqueous phase liquid (LNAPL) was monitored in an unsaturated subsurface soil of a field lysimeter under natural precipitation condition, and simulated with a two-dimensional numerical model to evaluate the potential as source of groundwater contamination. The microbial degradation of LNAPL in the soil was greatly enhanced after 90 days from the LNAPL contamination. The model was verified by comparison with the monitoring data of LNAPL residues after 14 and 28 days when the microbial degradation was not pronounced. However, the verified model, in which biodegradation with the first order kinetics occurred only in the aqueous phase, underestimated the microbial degradation from 28 days to 90 days, indicating the overestimation of the contaminant flux into groundwater. By assuming that the biodegradation occurred in both water and LNAPL phase in the contaminated soil, the verified model gave the simulation result with reasonable agreement with the monitoring data. The results suggested that evaluation of the behavior of LNAPL as source of groundwater contamination needed the appropriate estimation of the biodegradation in the LNAPL source zone.

**KEYWORDS;** lysimeter experiment; LNAPL; numerical simulation; source zone; biodegradation evaluation;

## 1. Introduction

Contamination of subsurface soil with petroleum hydrocarbons (HCs) which are present as light non-aqueous phase liquids (LNAPLs) is a serious environmental problem. Once released into subsurface environments, LNAPL often reaches the groundwater and leaves entrapped and residual LNAPL remaining in the vadose zone, and serves as a long-term source for groundwater contamination by releasing the relative soluble components such as benzene, toluene, ethylbenzene and xylenes (BTEX). Successful implementation of the remediation actions requires accurate evaluation of the behavior and fate of LNAPL contaminants in subsurface source zone, because the mass and distribution of LNAPL influences not only the time to achieve remediation objectives but also the potential for groundwater contamination and plume migration (U. S. EPA, 2004). Understanding of the mechanisms that control the behavior of LNAPL and the ability to predict the distribution and fate of LNAPL in source zone will contribute to the accurate evaluation and then the success of remediation efforts.

LNAPL such as gasoline or other fuel oil is a complex mixture with a wide range of physical and chemical properties. The transport behavior in subsurface with respect to advection, dispersion, partition and biodegradation are extremely complicated, which presented as problems of multiphase flow and multicomponent transport in vadose and saturated

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zones. Several models have been developed for simulating the behavior and fate of LNAPL in subsurface (Kaluvarachi and Parker, 1989; U.S. EPA, 1991). However, these rigorous models that simulate 2- or 3-dimensional flow and transport of LNAPL contaminants in the subsurface have extreme data requirements and are computationally intensive. This often results in uncertainty of prediction because of the difficulties to specify the required parameters, especially for biological processes since biodegradation rate data in vadose zone are very limited in literatures (Wiedemeier et al., 1999). In this paper, the migration, redistribution and fate of LNAPL released in subsurface are investigated by monitoring the processes in a field lysimeter experiment and numerical simulation. After verifying the migration of LNAPL phase and transport of total HCs in aqueous phase based on measurements, biodegradation processes in LNAPL source zone was investigated by comparing the results of simulation and observation in lysimeter experiment. An approach was proposed that would improve the accuracy of evaluation in source zone using simple and well-used first order decay model.

## 2. Site descriptions

The experiment was carried out using a field lysimeter in Nagoya University Farm, Togo-cho, Aichi Prefecture, Japan. The sides and bottom of the lysimeter are made of impermeable materials, and the surface is open to allow the precipitation infiltration, which is discharged into a 20 liter-volume tank by a drainage pipe (5cm in diameter) set at the bottom of the lysimeter (Fig. 1). During the experiment, the valve of the drainage pipe was kept open to make the lysimeter an unsaturated state.

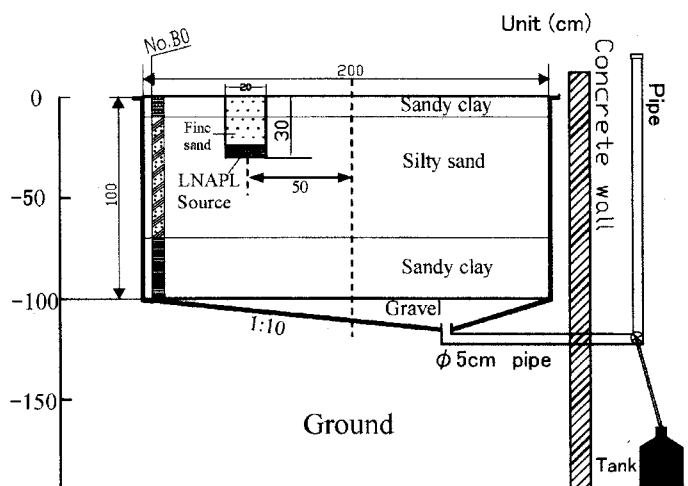


Fig. 1 Cross-section of lysimeter used in the experiment.

LNAPL were made by mixing HCs

of the following chemicals: toluene (15.5%, abbreviated as T), ethylbenzene (10.3%, abbreviated as E), (*o*-, *p*- and *m*-) xylene isomers (10.3%, abbreviated as X), naphthalene (5.2%, abbreviated as N) and *n*-dodecane (58.7%). The former 4 chemicals (TEXN) have higher aqueous solubilities than *n*-dodecane that is an inert component.

LNAPL was released into the bottom of a polyvinyl chloride pipe, which was buried with a depth of 30cm at the location of 50cm from to the horizontal center of lysimeter (Fig. 1). After total amount of 500 ml LNAPL was added, the pipe was immediately filled with fine sand to minimize the volatilization. During the period of experiment, soil samples from 20 cm below ground surface (BGS- 20 cm) to the bottom were collected as soil cores by a handy soil borer with an interval of 10 cm in depth after appropriate periods, and the HC concentration in soil was measured. The loss of HCs from lysimeter by volatilization was monitored at surface of lysimeter by adsorbing the HC gas with urethane form, and the loss of HCs as leachate by collecting discharged water in tank (Fig. 1). HCs in samples were extracted by *n*-hexane, and the concentration was determined by a gas chromatograph (Song and Katayama, 2005).

## 3. Numerical analysis of the filed lysimeter experiment

### 3.1 Numerical model

A 2-D integrated finite element model coupled with multiphase flow and multicomponent transport code MOFAT (U. S. EPA, 1991) was used to simulate the behavior of LNAPL in lysimeter. This program can be used to analyze three

phase gas(air)-LNAPL-water flow. The transport module can handle mass transfer of components in LNAPL among the water, gas and solid phases, and biodegradation with first order kinetics.

Assuming that the porous media is isotropic, and three phases, water, LNAPL, and gas, are incompressible, the governing equations for the flow of three phases are the mass conservation equations (Parker, 1989).

$$\phi \frac{\partial S_p}{\partial t} = - \frac{\partial q_{p,i}}{\partial x_i} + \frac{R_p}{\rho_p} \quad (1)$$

where  $\phi$  is porosity,  $S_p$  is the  $p$ - phase saturation, and  $p = a$  (soil gas),  $o$  (LNAPL) or  $w$  (water),  $x_i$  are Cartesian spatial coordinates ( $i, j = 1, 2$ ), and  $t$  is the time.  $q_{p,i}$  is the Darcy velocity of phase  $p$  in the  $i$ -direction,  $R_p$  is the net mass transfer into (+) or out of (-) phase  $p$ , and  $\rho_p$  is the density of phase  $p$ . In unsaturated soil, the relationships between capillary pressure heads ( $h$ ) and the saturation ( $S$ ) of phase  $p$  are described by the empirical function of *van Genuchten* (1980), and the relative permeability corresponding to the three phase *van Genuchten* model was used (U. S. EPA, 1991).

Assuming that LNAPL constituent can partition among water, LNAPL, soil gas and solid phases, the governing equations for component  $\alpha$  in phase  $p$  are given based on the mass conservation equations (Parker, 1989).

$$\phi S_p \frac{\partial C_{\alpha p}}{\partial t} = \frac{\partial}{\partial x_i} \left( \phi S_p D_{\alpha p, ij} \frac{\partial C_{\alpha p}}{\partial x_j} \right) - q_{p,i} \frac{\partial C_{\alpha p}}{\partial x_i} + R_{\alpha p} - \left( \mu_{\alpha p} + \frac{R_p}{\rho_p} \right) C_{\alpha p} \quad (2a)$$

where  $C_{\alpha p}$  is the concentration of the component  $\alpha$  in phase  $p$  expressed as the mass per phase volume [ $ML^{-3}$ ],  $D_{\alpha p, ij}$  is a tensor dispersion [ $L^2T^{-1}$ ],  $R_{\alpha p}$  is the net mass transfer rate of component  $\alpha$  into (+) or out of (-) the phase  $p$  [ $ML^{-3}T^{-1}$ ], and  $\mu_{\alpha p}$  is an apparent first-order decay coefficient [ $T^{-1}$ ] of component  $\alpha$  within phase  $p$ , which expresses the decay of component  $\alpha$  due to reaction such as biodegradation. To accommodate adsorption of components  $\alpha$  by the solid phase, an additional continuity equation for transfer of solid phase is required.

$$\frac{\partial C_{\alpha s}}{\partial t} = R_{\alpha s} - \mu_{\alpha s} C_{\alpha s} \quad (2b)$$

The phase transfer of component  $\alpha$  can be calculated by local equilibrium relation or nonequilibrium interphase transfer (U. S. EPA, 1991). MOFAT solves the systems of governing equations for multiphase flow and multicomponent transport using an efficient upstream-weighted finite element scheme. Nonlinear time integration in the flow analysis is handled using a Newton-Raphson method with an implicit saturation derivative formulation of the governing equations. The detail calculation algorithm, analysis approaches of the numerical model were described in Parker et al. (1987), Kaluarachchi and Parker (1989) and U. S. EPA (1991).

In this study, two phase flow, LNAPL and water flows, was dealt with. Mass transfer of components in LNAPL among the water, gas and solid phases was calculated by assuming local equilibrium relation and the concentration in LNAPL, water, gas and solid phase are given by the approximate thermodynamic relations (U. S. EPA, 1991). Soil gas transport was not considered, and soil gas was assumed to be present with an equilibrium state with water and solid phase under a constant pressure.

### 3.2 Site characterization and specification of simulation conditions

Parameters required for analyses of the two-phase flow are shown in Table 1, which were based on laboratory measurements or quoted from literatures. Bulk fluid properties were calculated based on composition of the used LNAPL mixture using the empirical relation (U. S. EPA, 1991). Physical and chemical properties of the LNAPL components for modeling component transport are quoted from literatures (Table 2). First order decay rate of the LNAPL components are

specified as the reported comprehensive value in unsaturated soil.

Two dimensional radial flow and transport module in the program (MOFAT) was used to simulate the LNAPL migration and component transports in lysimeter. The domain of the numerical model was defined as 100 cm in the depth and 50cm in radius (Fig.2). The surface was specified as flux boundary condition indicating the precipitation infiltration, and bottom side as specific water head (0 cm) boundary. Five hundred milliliters of LNAPL was introduced in the system by using injection function of the program (Fig. 2). The grid spacing of the model was set at 2.5cm. The net infiltration rate to precipitation was estimated from the difference between the total precipitation on surface area of the lysimeter and the observed discharged volume of water into the tank: 0.34 until 30 days after the LNAPL release and 0.25 after covering the surface of lysimeter with a nonwoven fabric for decreasing precipitation infiltration. The daily precipitation data (from Oct. 2003 to Feb. 2004) was obtained from a meteorological observatory near the site (Aichi-ken Agricultural Research Center, Nagakute, Aichi Prefecture, Japan).

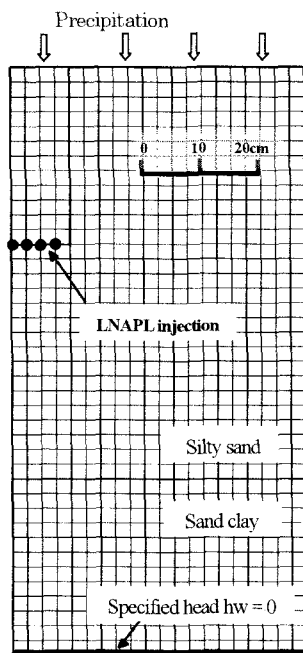


Fig. 2 Model description

Table 1 Parameters of unsaturated soils and NAPL phase

Unsaturated soil parameters	Sand in source	Silty sand	Sandy clay
<sup>a</sup> Saturated conductivity $K_s$ (cm/day)	$3.4 \times 10^{-2}$	$5.0 \times 10^{-3}$	$3.4 \times 10^{-4}$
<sup>a</sup> Porosity $\phi$	0.39	0.44	0.48
<sup>a</sup> Bulk density $\rho_b$ (g/cm <sup>3</sup> )	1.47	1.48	1.4
<sup>a</sup> Organic carbon content $f_{oc}$	0.14%	0.14%	0.14%
<sup>b</sup> Residual water saturation $S_m$	0.1	0.14	0.19
<sup>b</sup> Van Genuchten $\alpha$ (1/cm)	0.145	0.124	0.027
<sup>b</sup> Van Genuchten $n$	2.68	2.28	1.23
<sup>c</sup> Maximum residual NAPL saturation $S_{or}$	0.20	0.20	0.20
<sup>d</sup> Longitudinal dispersivity $\alpha_L$ (cm)	$5.3 \times 10^{-2}$	$5.3 \times 10^{-2}$	$5.3 \times 10^{-2}$
<sup>d</sup> Transverse dispersivity $\alpha_T$ (cm)	$5.3 \times 10^{-3}$	$5.3 \times 10^{-3}$	$5.3 \times 10^{-3}$
NAPL Properties		Value	Reference
Scaling parameter $\beta_{ao}$	3.25	Calculated based on composition of the NAPL phase using the empirical relation (EPA, 1991).	
Scaling parameter $\beta_{aw}$	1.75		
Specific gravity $\rho_{ra}$	0.80		
Relative viscosity $\eta_{ra}$	1.12		

- a Measured data using soil samples from lysimeter before the LNAPL release, and  $f_{oc}$  is measured data of sandy clay since only one value can be used as input.  
b From Carsel and Parrish (1988).  
c Typical value for sandy soils from U.S. EPA(1991).  
d Approximated by measured average grain size ( $D_{50}$ ) of silty sand (Tamai and Kawanishi, 1998) since only one value can be used as input, and assuming  $\alpha_L/\alpha_T = 10$ .

Table 2 Physical and chemical properties of LNAPL components used in the experiment

Property		Toluene	Ethylbenzene	Xylenes	Naphthalene	n-dodecane
<sup>a</sup> Diffusion coefficient (cm <sup>2</sup> /s)	in water	$9.4 \times 10^{-6}$	$8.5 \times 10^{-6}$	$8.5 \times 10^{-6}$	$9.4 \times 10^{-6}$	$9.4 \times 10^{-6}$
	in air	$8.5 \times 10^{-2}$	$7.6 \times 10^{-2}$	$7.2 \times 10^{-2}$	$7.2 \times 10^{-2}$	$8.5 \times 10^{-2}$
	in LNAPL	1.40	1.08	0.91	0.55	0.55
<sup>a</sup> Water solubility (mg/cm <sup>3</sup> )		0.515	0.152	0.198	0.033	$3.7 \times 10^{-6}$
<sup>a</sup> Henry's constant		0.26	0.32	0.29	0.049	530.76
<sup>b</sup> Oil-water partition coefficient $\Gamma_{ow}$		1683.5	5703.9	4444.4	35212.1	202702.7
<sup>b</sup> Solid-water partition coefficient $\Gamma_{os}$		0.28	0.20	0.50	2.67	1433
<sup>c</sup> Decay coefficients $\mu_{ap}$ (1/day)		$2.48 \times 10^{-2}$	$3.00 \times 10^{-3}$	$1.90 \times 10^{-3}$	$2.70 \times 10^{-3}$	$2.48 \times 10^{-2}$

a From U. S. EPA(1991) except for n-dodecane, which is from Demond and Lindner (1993).

b Calculated based on relation with organic carbon content in soil (U. S. EPA,1991).

c From Wiedemeier et al. (1999), and n-dodecane was assumed to have the same value as toluene.

#### 4. Results and Discussion

##### 4.1 Verification of the numerical model

The model was verified using parameters shown in Tables 1 and 2 by comparing the simulation results with the observed HC concentration in soil at 14 days and 28 days after LNAPL release. The simulation was to verify the

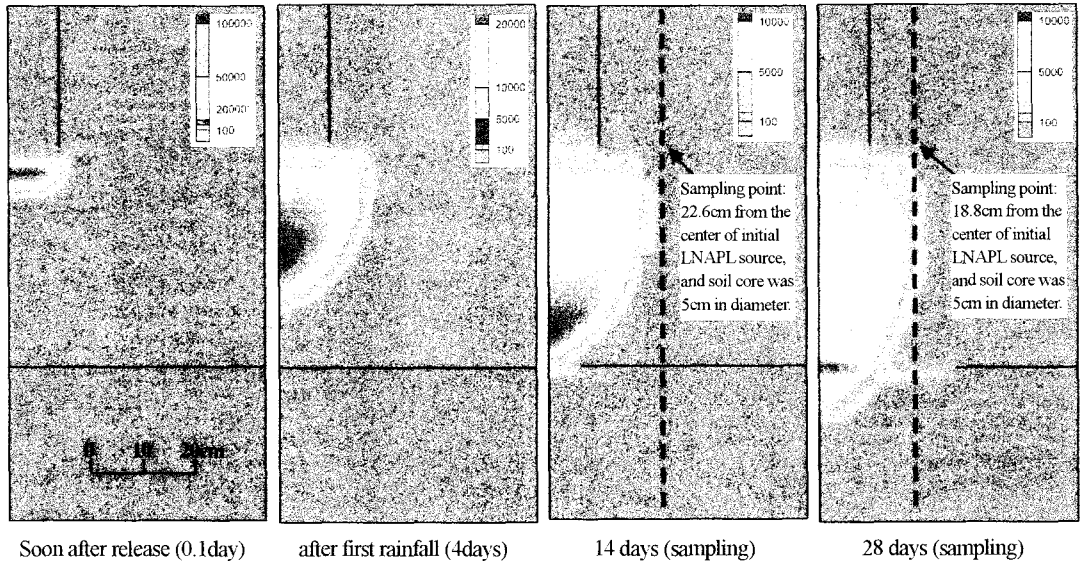


Fig. 3 Concentration of total HCs in NAPL phase indicating the migration of LNAPL after release in subsurface

migration of LNAPL phase and the transport of the HC components in LNAPL with assumption of no biodegradation, which influences were considered to be not significant in the early period. The field measurement showed that the loss by volatilization and leaching was negligible after 28 days (Song et al., 2004). At 14 days after LNAPL release, the measured HC concentration in soil samples were  $10^0$ - $10^1$  mg/kg DS (DS means dry soil), and the main components were TEX, which occupied 40-45% of total HCs at BGS-20-40cm, and over 75% below BGS-40cm. LNAPL did not migrate to the sampling point. The simulation results also show that LNAPL phase has almost but not reached the sampling point (Fig. 3). The simulated HC concentration ranges from  $10^0$  to  $10^1$  mg/kg DS with TEX as the main components, except for the results at BGS-30-40cm where the average HC concentration is estimated as over  $10^2$  mg/kg DS (Fig. 4). This overestimation would be due to the overlap with the front of LNAPL phase. At 28 days after LNAPL release, the measured HC concentration in soil samples were over  $10^3$  mg/kg

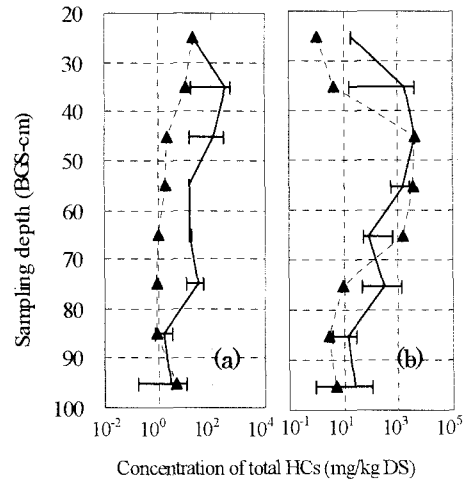


Fig.4 Verification of numerical model. (▲) indicates observed HC concentration in soil at (a) 14 days and (b) 28 days. The horizontal bars in the simulation results indicate the maximum and minimum value in sampling position.

DS at BGS-40-70 cm with a maximum of 4,500 mg/kg DS. The main component was *n*-dodecane which occupied 80-90% of total HCs, suggesting that LNAPL phase had reached to the sampling point. The simulation also shows that LNAPL phase has reached the sampling point (Fig. 3), and that the simulated HC concentration ranges over  $10^3$  mg/kg DS with a maximum of 4,400 mg/kg DS (Fig. 4). The simulated concentration profile along with depth was similar to the measured one although there were some deviations. Considering the complexity of LNAPL migration under natural precipitation conditions and the heterogeneity of HC distribution in field lysimeter, the simulation results were considered to be in reasonable agreement with the field observation.

#### 4.2 Evaluation of biodegradation in LNAPL source zone

Soil samples were collected at 14, 28, 62 and 92 days after the LNAPL release, from the locations in the range from 15 to 19 cm from the center of initial LNAPL source except for those after 14 days when the samples were collected at 22.5cm from the source center. The field monitoring of HCs showed that only 1% of added HCs were lost due to volatilization and leaching with infiltration water during 90 days of the experiment (Song et al., 2004). This suggested that the loss of HCs from lysimeter due to volatilization and leaching was negligible, and the pronounced decrease of total HCs after 92 days indicated the biodegradation in LNAPL source.

For describing the biological processes in detail, rigorous models such as Monod model are suitable, but these models need large numbers of parameters to be verified. Since less information is available due to the site-specific properties of biodegradation processes, simple first order decay rate model (U. S. EPA, 1991) has been commonly used and considered to be practical in real contamination sites. In this study, a numerical, two-dimensional radial model with first-order decay kinetics coded as MOFAT (U. S. EPA, 1991) was applied to simulate the biodegradation in the LNAPL source zone.

The residual LNAPL phase serves as groundwater contamination source by the release of dissolved components (TEXN in case of this study) into groundwater due to precipitation infiltration. The soil with LNAPL phase (BGS-40-70cm) was regarded as the source zone, and the dissolved components of TEXN were considered to be leached into the underlying soil (BGS-80-100cm). Therefore, the simulation was performed considering different biodegradation processes in these two soil zones.

Four cases of simulation were carried out by considering different biodegrading processes. Case 1 considered that biodegradation occurred only in water phase, and used decay rate from literatures (Table 2). This is commonly used method especially in real sites where less information is available concerning on the biodegradation. In Case 2 and Case 3, the decay rates in water phase were specified to be by 2 folds and 10 folds larger than that in Case 1, respectively. The decay rates of Case 3 were larger than the highest values of first order decay rates reported (Aronson and Howard, 1997): toluene 0.059; ethylbenzene 0.015; xylenes 0.021. In Case 4, biodegradation was assumed to occur in water phase and also LNAPL phase from 28 days after the LNAPL release. Case 4 used the highest decay rates of TEX in water phase described above, and decay

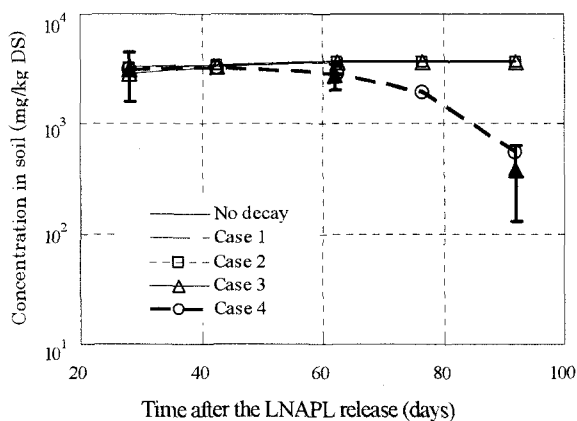


Fig.5 Observed and simulated HCs concentration at NAPL source zone (BGS-40-70cm) considering different biodegradation processes. Symbol  $\blacktriangle$  indicates the average of the observed HCs concentration with vertical bars indicating the maximum and minimum. Simulated results were the total HCs concentration averaged within sampling position (15 to 19cm from the center of initial LNAPL source).

rate of naphthalene was assumed to be 0.027, n-dodecane the same as toluene.

The simulation of biodegradation under the conditions of Case 1, Case 2 and Case 3 did not fit to the observed results. The simulated HC concentration in LNAPL source zone shows little degradation, suggesting that the pronounced dissipation of HCs in the source zone after 62 to 92 days cannot be described by the biodegradation in water phase only, even using very high decay rates such as in Case 3 (Fig. 5). Fig. 6 shows the simulated and observed TEXN concentration in underlying soil (BGS-80-100cm) below LNAPL source zone. Using high decay rates in water phase only, low concentration of TEXN is calculated in underlying soil during early period, but the simulation shows the similar trend of

increasing HC concentration with time in the three cases, which does not agree with the observed results. The simulation results by assuming the biodegradation in both water and LNAPL phases (Case 4) well fits with the observed results of the remaining HC concentration (Fig. 5), where the decay rate in LNAPL phase was set at  $0.005 \text{ day}^{-1}$  by a trial and error method. The simulated TEXN concentration in underlying soil was also in well agreement with the observed results, which were in a range of 1 to 2 mg/kg DS (Fig. 6), during 40 days to 92 days after LNAPL release.

These results suggested that considering biodegradation only in water phase would fail to evaluate the behavior and fate of LNAPL in source zone, and overestimate the HC concentration in the leachate from the residual LNAPL phase. The results of Case 3 which supposed 10 folds decay rate in water phase are still not in agreement with field measurements in both LNAPL source zone and the underlying soil. The simulation under the conditions of the biodegradation in LNAPL phase as well as in water phase agreed well with the observed results, even using simple first order decay model in MOFAT.

The biodegradation of HCs in LNAPL phase has been indicated by various observations although any simulation model has not incorporated it. The microbial biomass in soil contaminated with high HC concentration increased more than two folds than that of uncontaminated soils in the lysimeter (Kitamura, et al., 2004), indicating the biomass increase by the consumption of HCs in LNAPL phase. It has been reported that even hydrocarbons with very low water solubility can be degraded (Alexander, 1994), and alkanes that contained up to at least 44 of carbon atoms can be degraded even with a solubility lower than  $10^{-3} \text{ mg/L}$  (Haines and Alexander, 1974). It has been also indicated by the report that the maximum rate of biodegradation of contaminants in NAPLs cannot always be predicted from the rate of their spontaneous partitioning to water (Efroymson and Alexander, 1994).

## 5. Conclusions

This study investigated the behavior of LNAPL after the release into subsurface soil by a field lysimeter experiment and numerical simulation. Using the parameters based on laboratory measurements and literatures, a numerical, two-dimensional radial model was verified with a reasonable agreement with migration and redistribution of LNAPL phase of the field observation during a period of 28 days after the LNAPL release, when microbial degradation was not

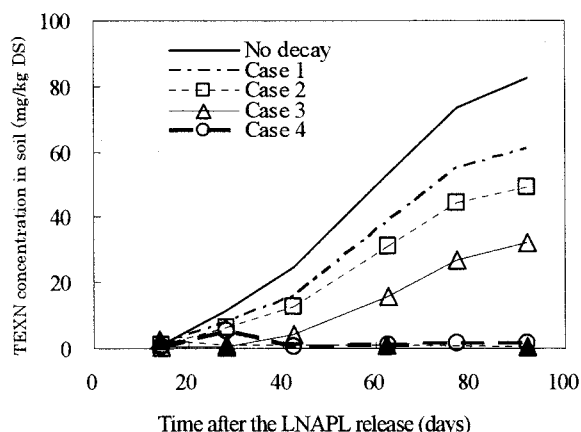


Fig.6 Observed and simulated TEXN concentration in soil (BGS-80-100cm) below LNAPL source zone by considering different biodegradation cases. Symbol  $\Delta$  indicates the average of the observed TEXN concentration with vertical bars indicating the maximum and minimum at BGS-80-100cm. Simulated results were the TEXN concentration averaged within sampling position (15 to 19cm from the center of initial LNAPL source).

pronounced. For long term behavior of residual LNAPL, biodegradation became the most important factor, and biodegradation processes using the practically-used first order decay model showed that considering biodegradation in water phase only will fail to evaluate the biodegradation rate of LNAPL in source zone, and resulted in overestimation of the release of dissolved contaminants into groundwater. This problem can be overcome by considering the biodegradation in LNAPL phase, simulation results are in a well agreement with field observation, and may provide more accurate estimation of the release of dissolved HCs from LNAPL source. The results also suggested the limitation of using first-order decay model to evaluate the biodegradation process in LNAPL source zone. As the biodegradation occurred, microbial biomass showed increase in LNAPL source zone (Kitamura et al., 2004), and this results in the increase of biodegradation rate. The results by first-order decay model tend to underestimate the biodegradation rate in LNAPL phase since it does not take the change in microbial biomass into account. Further investigation based on increased microbial biomass is currently being carried out to evaluate the biodegradation process accurately in source zone soils.

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