NUMERICAL MODELING FOR ASSESSMENT OF CONTAMINANT VERTICAL DISTRIBUTION UNDER PARAMETER UNCERTAINTIES

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The assessment of discharge rate and discharge period of dioxins and chlorobenzene which have contaminated the subsurface systems beneath O River, in O City is undertaken through the development of one dimensional transport model employing method of characteristic. The developed model is designed to couple the process of advection, dispersion and retardation of chlorobenzene in vertical direction representing the transport of other contaminants in the site. A variety of scenario based on mass flux and fraction of organic carbon of soil (F_{oc}) was applied to allow the use of a number of uncertain parameters. The most reasonable simulation result indicated that the contaminants were likely to be released since 1930s until 1975, whereas the transport has been taking place until now. Moreover, the integrated modeling approach may reveal that the migration of hydrophobic compounds (i.e. dioxins) can be significantly enhanced in the presence of a solvent (i.e. chlorobenzene).

Key Words : *dioxins , chlorobenzene, discharge rate, discharge period, transport model*

1. INTRODUCTION

Thorough understanding of the simultaneously occurring processes in contaminated groundwater systems is needed prior to designing an appropriate monitoring and remediation measure. Nevertheless, a variety of uncertainties pertaining to hydraulic properties, and contamination mechanisms and behaviors has been involved in contaminated sites around the globe. It has been noted as well that most contamination history in particular concerning with pollutant discharge rate and period, is commonly unrecorded. These valuable information are necessary not only for accurate site characterization but also for supporting environmental regulatory measures. Numerical modeling has become a worthwhile tool nowadays employed to support both practitioners and scientists in such a formidable task.

One example of developed numerical code for estimating contaminant mass flow rate is CSTREAM. This particle tracking-based numerical algorithm is designed to enable quantification of contaminant mass flow rates in aquifer. Despite some simplifying provides a range of mass flow rate estimates that may be effectively used for the assessment [1)]. However, it needs a number of measured concentration time series observed during pumping tests at several wells.

The objective of this study is to develop the one dimensional numerical model for predicting the natural vertical transport and fate of multi species of chlorinated organic compounds within the two different porous media layers. The developed model coupled the processes of advection, dispersion, and sorption using method of characteristic. This model was applied to analyze the mass transport under a range of scenario of the discharge rate and discharge time length of dioxins and chlorobenzene in O River, O City, Japan, considering the lack of required data.

2. DESCRIPTION OF THE SITE

(1) Groundwater hydraulics of the site

The structural properties of aquifer in the area of interest (i.e. size, location, and amount of clay lenses, sand and gravel layers, and resulting heterogeneous distribution of hydraulic conductivity and porosity) like in most aquifers significantly control

groundwater flow and spreading of solutes [2]. The contaminated site is composed by interconnected two alluvial layers in which silty clay of 2.3 m thick and sand of 3.7 m thick are the predominant material of the first and second layer, respectively. The parameters used in the study can be seen in **Table 1**.

The gravitational effect of density of contaminants most probably acts as the main driving force in the one dimensional downward transport of chlorinated organic compounds which can be expressed as follows:

$$V_y = -K_{sat} \times \left(\frac{\partial h}{\partial y} + \frac{\rho_{coc}}{\rho_f} \right) \quad (1)$$

where V_y, K_{sat}, $\partial h/\partial y$, ρ_{coc}, and ρ_f denote vertical mean velocity in downward direction, saturated permeability, water pressure head gradient, organic compound density and fresh water density, respectively. Assuming the static pressure head gradient, Eq.(1) then changes to:

$$V_y = -K_{sat} \times \left(\frac{\rho_{coc} - \rho_f}{\rho_f} \right) \quad (2)$$

(2) Contamination conceptual model

The assessment of dioxins survey throughout Japan conducted by Ministry of Environment in 2000 indicated that relatively high concentrations of dioxins in sediment of public waters were identified. In the same way, the concentrations of dioxins at surveyed soil points were above survey index value, despite the fact that these points met the environmental quality standard for soil [3].

The detailed investigation of contamination in O River revealed the presence of dioxins, Polychlorinated Byphenyls (PCBs), chlorobenzene (CB), Pentachlorophenols (PCPs) and Polycyclic Aromatic Hydrocarbons (PAHs) in the soil under the riverbed concrete. Even though the river bed was concreted, the pollutants should seep out from groundwater to the river. The measured data provided in this investigation was influenced by pumping done by the suspected factory to remediate the contamininated site.

Dioxins, or chlorinated dibenzo-*p*-dioxins (CDDs), are a class of structurally similar chlorinated hydrocarbons. The basic structure is comprised of two benzene rings joined via two oxygen bridges at adjacent carbons on each of the benzene rings. There are eight homologues of CDDs, monochlorinated (the least chlorinated homologous) through octachlorinated (the most chlorinated homologous). Each homologous group contains one or more isomers or congeners [4]. This chemical group is commonly generated as unwanted by-products in many industrial processes. In the contaminated site the leastthree chlorinated dioxins (TrCDD, DCDD and MCDD) are not detected.

Table 1 The parameters used in the study

Parameters	Unit	Layer 1	Layer 2
Dominating Material		Silty clay	Sand
Depth	cm	230	370
Density of chlorobenzene	g/cm^3	1.2	1.2
Density of water	g/cm^3	1.00	1.00
Porosity	-	0.2	0.15
Saturated Permeability	cm/sec	1.0 E-5	1.0E-3
Pore velocity	cm/sec	6.0E-05	8.0E-03
Grain size	cm	5.0E-04	9.0E-03
Molecular diffusion coefficient	cm^2/sec	1.0E-05	1.0E-05
Longitudinal dispersivity	cm	5.0E-04	9.0E-03
Soil density	g/cm^3	2.643	2.645
Bulk density	g/cm^3	2.115	2.5
Fraction of organic carbon content (F_{oc})	%	0.24 – 0.70	0.16

The mobility and bioavailability of organic contaminants associated with beds depend on the concentrations of these compounds in pore water. These pore water concentrations, in turn, are controlled by sorption of the contaminants to the sediment solids. Additionally, non polar organic compounds are believed to sorb to sediment particles as a result of partitioning of the compounds between pore water and the sediment organic mater [5].

In the site, due to their extremely high hydropobicity, dioxins and PCB are most probably to strongly adsorb to the soil material instead of moving downstream once they were introduced into subsurface system. Similarly, the decrease concentration of the more chlorinated dioxins associated with the increase concentration of the lesser chlorinated dioxins along the depth of two different soil materials can not be obtained by the simulated vertical transport model, as a result of dioxin low solubility and high fraction of organic carbon of the material [6]. It can be noted as well that the simulated apparent velocity of octachlorinated dioxins (OCDD) was 5.5 x 10^{11} times slower than pore water velocity.

However, positive correlation between concentrations profile of dioxins and PCB with that of CB was demonstrated by the measured data [7]. It then can be realistic to assume that dioxins and PCB are dissolved and transported in chlorobenzene as shown in **Fig.1**

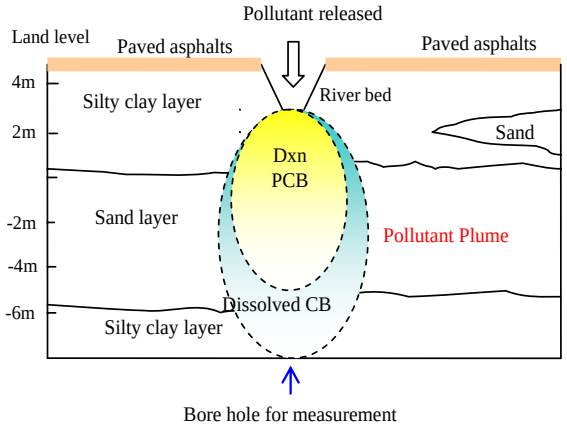

Fig.1 Schematic illustration of the site contamination.

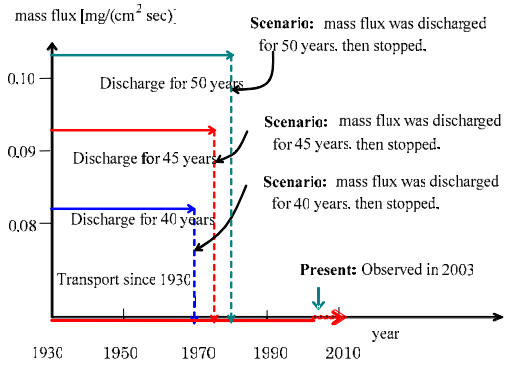

Fig.2 Mass flux based scenarios

3. MODELING METHOD

(1) Mathematical Model

The governing equation describing the change of concentration due to advection, dispersion, and reaction can be expressed as follows [8]:

$$\frac{\partial C}{\partial t} + V_y' \frac{\partial C}{\partial x} = D_L \frac{\partial^2 C}{\partial x^2} - \frac{\partial q_s}{\partial t} \qquad (3)$$

where C is solute concentration (ML^{-3}) and q_s is concentration on solid (expressed in term of pore water concentration = ML^{-3}).

The longitudinal dispersion coefficient reflecting contaminant spreading in the vertical direction can be obtained by this calculation [9]:

$$D_L = \alpha_L \times \left| V_y' \right| + \tau D_M \qquad (4)$$

where D_L, α_L, τ and D_M are longitudinal dispersion coefficient, longitudinal dispersivity, tortuosity and molecular diffusion coefficient, respectively. The grain sizes estimated from the isotropic intrinsic permeability value using the Kozeny-Carman equation are used to approximate longitudinal dispersivity values [10]. Tortuosity [11] is considered equal to 1, whereas the molecular diffusion coefficient is equal about 10^{-5} cm^2/sec [12].

The sorption term accounting for the delay of contaminant transport as a result of sorption into soil material or sediment can be incorporated by replacing $\partial q_s / \partial t$ by retardation factor which is puted using the following equations:

$$R_k = 1 + Kd_k \left(\frac{\rho_b}{\theta} \right) \qquad (5)$$

$$Kd_k = K_{oc,k} . F_{oc} \qquad (6)$$

$$\log K_{oc,k} = \log K_{ow,k} - 0.35 \qquad (7)$$

where R_k, Kd_k, $K_{oc,k}$, $K_{ow,k}$, ρ_b, θ and F_{oc} denote retardation factor of the k-th species, the distribution coefficient (LM^{-3}) that depends on the solute species, the octanol-carbon partitioning coefficient and the octanol-water partitioning coefficient of the k-th species, the density bulk of the sediment (i.e. the ratio of mass of dried soil to total volume of the soil in ML^{-3}), porosity and the fraction of organic carbon, respectively [8]. Thus equation (3) is changed to:

$$\frac{\partial C}{\partial t} + \frac{V_y'}{R_k} \frac{\partial C}{\partial x} = \frac{D_L}{R_k} \frac{\partial^2 C}{\partial x^2} \qquad (8)$$

Since the measured data of contaminants are expressed in sorbed concentration, linear isotherm equation reflecting equilibrium partitioning process is applied as follows:

$$\tilde{C}_k = Kd_k . C_k \qquad (9)$$

where C_k is the aqueous-phase concentration of the k-th species (ML^{-3}), $\tilde{C}_k$ is the solid-phase concentration of the k-th species (MM^{-1}).

(2) Numerical Approach

In this study, equation (8) is solved by Method of Characteristic (MOC).

A saturated one dimensional porous media of 6 m thick was discretized by 10 cm cells. The mass flux boundary condition was assigned at the top of model domain, meanwhile the gradient of concentration equal to zero was prescribed at the bottom boundary ($\partial C / \partial y = 0$). In addition, no pollutant background was specified in the intial condition.

The advection-dispersion MOC code [13] was modified to simulate 70 year of transport of chlorobenzene representing the transport of 5 dioxin homologues under the various scenarios of pollutant discharge rate, discharge period and fraction of organic carbon of material. The result of previous simulation indicated that the change of pollutant concentration profile was attributed to the change of those three parameters [6]. The transport scenarios performed in this study is presented in **Fig.2**.

4. RESULT AND DISCUSSION

The developed model was calibrated operating 7 dissimilar cases by which discharge rate of 0.08, 0.09 and 0.1 mg/(cm^2 sec), discharge period of 40, 45, 50 years, and F_{oc} of 0.4%, 0.5% and 0.6% were used. In the meantime the transport time of 70 years was performed for the whole cases. Those simulation results based on that mass flux and F_{oc} scenarios can be summarized as follows.

The different CB concentration profile due to slight change of discharge rate can be demonstrated as given in **Fig.3**. Whereas **Fig.4**. presents the diverse of concentration profile of CB as a range of discharge period was employed. The simulation result of F_{oc} -based scenario indicates that the pattern of CB concentration profile is distinctly deviated as various F_{oc} values were used as seen in **Fig.5**.

The immediate alteration of profile behavior of contaminants at the border of two different soil materials can be well demonstrated by the developed model. Moreover, it can be observed that this behavior is significantly influenced by F_{oc} contained in the first layer than by other parameters.

The case at which discharge rate of 0.08 mg/(cm^2 sec), discharge period of 45 years and F_{oc} of 0.5% is observed as the most reasonable case. It may be interpreted that the pollutants was continuously released since approximately 1930s until 1975, while the transport has been occurring until now. This profile of concentration with respect to depth during 70 years of transport based on that selected case is depicted in **Fig.6**.

It is worthwhile to note that the measured data used for calibration was affected by pumping effort carried out to clean up the contaminants. Since the developed model did not consider that pumping work, the obvious deviation between the simulated result and the measured data is observed.

The comparison between measured and calculated dioxins can be approached by converting the aqueous-phase of calculated CB to the sorbed-phase. The ratio of measured CB and the asured dioxins is then used to acquire the sorbed-phase of predicted dioxins. The measured and predicted of dioxins are shown in **Fig.7**. Furthermore, the predicted discharge rate of monochlorinated to octachlorinated dioxins were computed using that ratio in **Table 2**.

Due to their low solubility rate and high fraction of organic carbon contained in the soil material, dioxins preferebly adsorb to the soil, instead of mobilizing to the further downstream. However, the measured data signified that significant concentration of dioxins was found downstream. Thus the simulated result may prove that the mobilization of

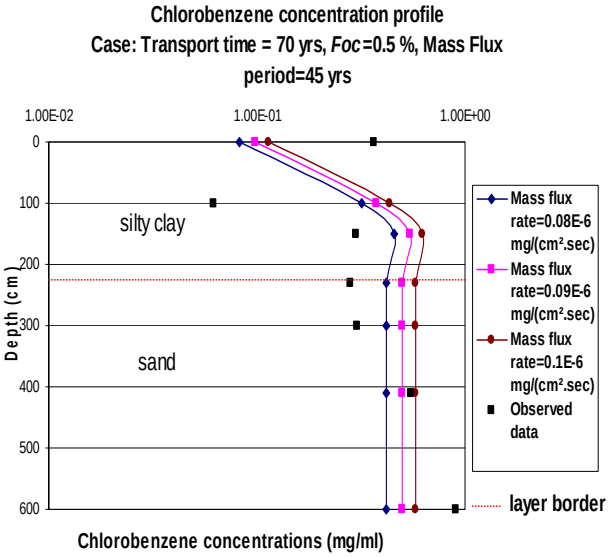

Fig.3. Mass flux rate scenario.

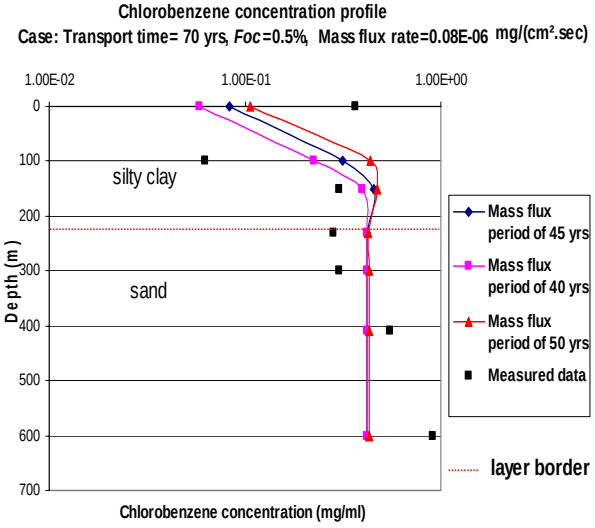

Fig.4. Mass flux period scenario.

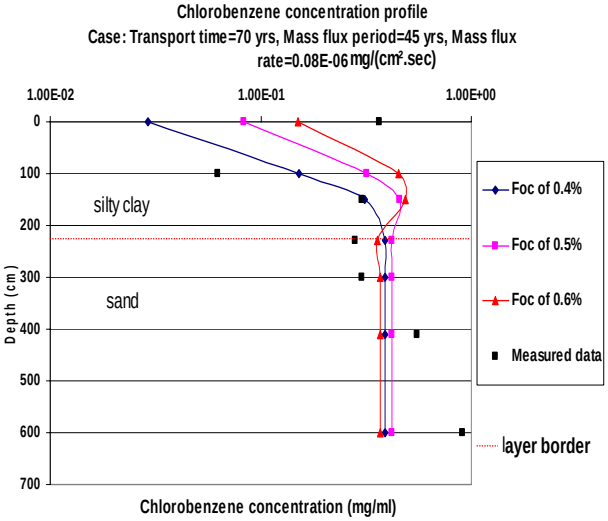

Fig.5. F_{oc}-based scenario.

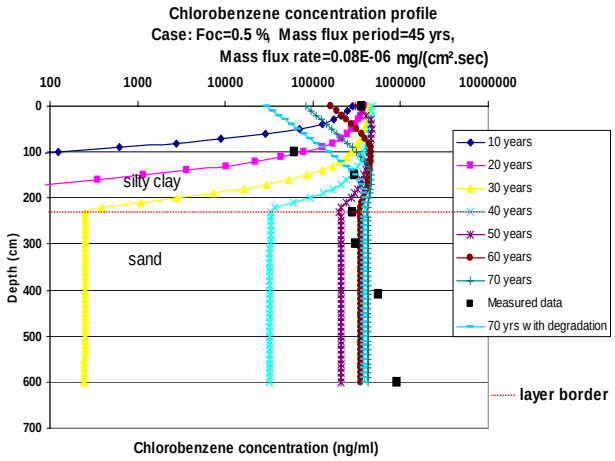

Fig.6. Concentration profile of CB with time

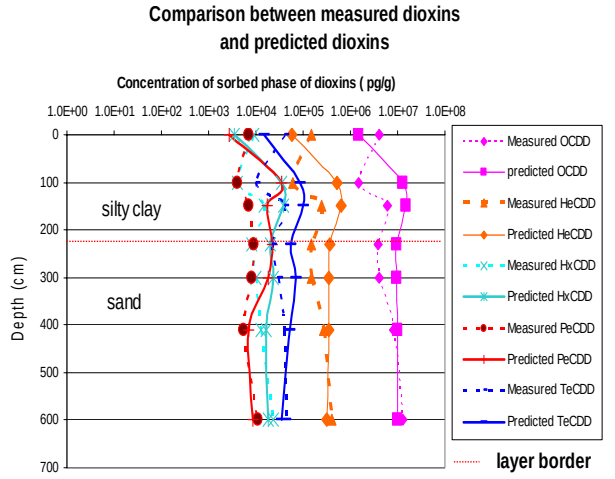

Fig.7. Concentration profile of measured and predicted dioxins

Tabel 2 Predicted discharge rate of dioxin homologues

Dioxin homologues	Discharge rate (p g/(cm^2 sec)
OCDD	0.1
HeCDD	0.387
HxCDD	0.0232
PeCDD	0.0186
TeCDD	0.001

hydrophobic contaminants like dioxins can be significantly enhanced in the present of a solvent like CB. It is supported as well by the fact that the positive correlation between measured dioxins and CB was discovered in the site [7].

5. CONCLUDING REMARKS

Generally, there is a little information on the study of transport of dioxins in groundwater which can be used to validate the numerical model. The present data would be one of such available field investigation.

The developed model can successfully show the effect of the density of CB in driving the contaminants downward. The change of profile behavior of contaminant concentrations due to the use of a range of affecting parameters can be also well demonstrated.

The sensitivity analysis undertaken by carefully observing the profile behavior of concentration revealed that F_{oc} was the most sensitive parameter, whereas mass discharge time period and mass flux rate show approximately similar sensitivity toward the distribution of concentration.

The pumping recently done to remove the contaminants was most probably to result in the deviation of profile pattern between the measured dioxins and CB and the predicted ones.

Moreover, the discharge rate and discharge period of dioxins can be adequately estimated employing the integration of MOC -based model and the assumed scenarios.

This modeling approach can be useful for a preliminary assessment of the distribution of dioxins, and CB in the vertical direction, particularly under condition in which the availability of data is very limited. A two or three dimensional flow and transport modeling taking into account both natural and man induced processes should be done in the future to support in the better way the assessment of contaminant plume development in the site.

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