

Numerical Transport Model of Chlorinated Organic Compounds in Saturated Porous Media

by

Budi KURNIAWAN* and Kenji JINNO**

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Abstract

The wastes resulting from various activities combusting and processing chlorine containing organic materials have contaminated groundwater systems in many places over years. Prediction of distribution and fate of those contaminants need to be obtained prior to designing an appropriate monitoring and remediation scheme. In this study, a solute transport model was developed to simulate the simultaneously occurring processes of multi-species chlorinated organic compounds which were transported through multi-layers of saturated porous media. The model simulation result of dioxin transport in groundwater indicated that there was no significant dioxin concentration throughout the model domain after being transported for 50 years. Chlorobenzene transport simulation representing other species of contaminants was performed due to the fact that in the contaminated site the chlorobenzene transport in groundwater most likely can transport dioxins and other chlorinated organic compounds. The results of this transport simulation demonstrated that fraction of organic carbon content of material (F_{oc}), mass flux magnitude of contaminants, and contaminant discharge period were the most important parameters which affected the distribution of contaminant concentration. In addition, the profound change of the pollutant concentration profile was distinctly observed as the change of F_{oc} was given. Thus developed model particularly can be used to carry out a preliminary estimation of the mass flux magnitude and the mass flux period.

Keywords: Dioxins, Chlorobenzene, Contaminant transport model, Mass Flux

* Graduate Student, Department of Urban and Environmental Engineering

** Professor, Department of Urban and Environmental Engineering

1. Introduction

Dioxin is the most common name given to the group of molecules made up of two chlorinated benzene rings connected by one or two atoms of oxygen which have been generated as unwanted by-products in many industrial processes. In general, these compounds have very low water solubility, high octanol-water partition coefficients, and low vapor pressure ¹⁾.

A survey for dioxin in the Omuta River was jointly conducted in 2000 by Japan's Ministry of the Environment and the Fukuoka Prefectural Government ²⁾. It revealed the exudation of oil droplets of high dioxin contents through riverbed concrete joints and demonstrated the presence of dioxin containing soil under the riverbed concrete.

The integration of characterization of the field site consisted of hydrogeo-chemistry and contaminant properties to figure out the relative importance of simultaneously occurring processes which affected the distribution of the contaminants is indispensable prior to employing monitoring and remediation related decisions. Numerical solute-transport models have been developed world wide to simulate distribution and fate of various pollutant types in porous media.

The solute transport and biodegradation code BIOMOC by U.S. Geological Survey (USGS) was used in conjunction with the USGS universal inverse modeling code UCODE to quantify field-scale hydrocarbon dissolution and biodegradation at the USGS Toxic Substances Hydrology Program crude-oil spill research site located near Bemindji, MN, USA ³⁾. BIOMOC is a two-dimensional, multi-species reactive solute-transport model with sequential aerobic and anaerobic degradation processes. In that study the transport was simulated using the particle-based Method of Characteristics ⁴⁾.

Rifai et al. (1987) developed a two-species bioremediation model, known as BIOFLUME-II, to predict fate and transport of hydrocarbon contaminants that degrade via aerobic reaction ⁵⁾. The model was recently updated to describe other anaerobic reaction mechanism for modeling hydrocarbon decay processes.

Clement (1997) and Clement et al. (1998) developed a multi-species reactive transport code called RT3D for simulating bioremediation in subsurface environments ^{6),7)}. Unlike other bioremediation simulation codes, RT3D is a general-purpose reactive transport solver that can be used for solving any number of transport equations that are coupled with any type of biochemical kinetics.

The objective of this study is to develop a one dimensional numerical model for predicting naturally vertical transport and fate of multi species of chlorinated organic compounds within the two different saturated porous media layers. In particular the developed model coupled the processes of advection, dispersion, sorption and biodegradation applying Method of Characteristic (MOC). This model was purposed as a preliminary effort particularly to estimate the contaminant source rate and discharge time length which was not included in those mentioned programs.

2. Conceptual Model

Bear and Veruijt (1998) stated the conceptual model consists of a set of assumptions that reduce the real problem and the real domain to simplified versions that are acceptable in view of the objectives of the modeling and of the associated management problem ⁸⁾. Similarly Bredehoeft (2005) suggested that the conceptual model is the basic idea, or construct, of how the system or process operates; it forms the basic idea for the model (or theory) ⁹⁾. Mathematically, a conceptual model is nothing more than a set of assumptions that relate to items such as boundary conditions, initial conditions, geological description, flow regime, source/sink distribution, hydraulic

conductivity distribution, transport parameters, and other flow and transport parameters¹⁰⁾. The following sections describe a set of assumption employed at the area of interest consisting of the schematization of hydrogeology system and the concept of mathematical model.

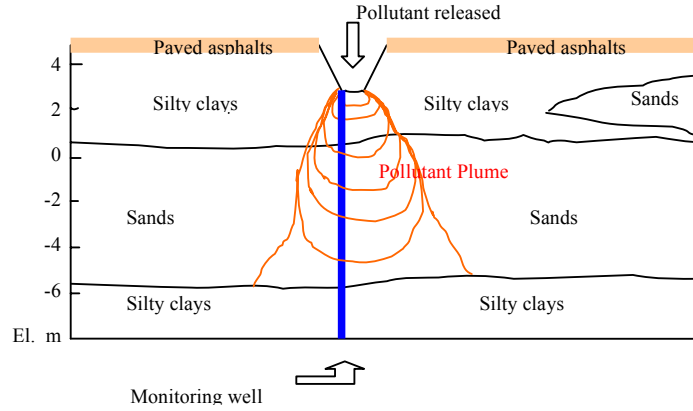


Fig.1 Contaminated site description.

2.1 Hydrogeology system of the site

The area of interest is made up of interconnected two alluvial layers in which for the first, and second layer are predominated by silty clay, and sand, respectively. The contaminated site description is depicted in **Fig.1**. The following equation was employed to govern the one dimensional downward transport of dioxins including the gravitational effect of the density.

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

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

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

The grain sizes were estimated from the isotropic intrinsic permeability value using the Kozeny-Carman equation¹¹⁾. The obtained grain sizes were then used to approximate longitudinal dispersivity values. Subsequently these values were applied to calculate longitudinal dispersion coefficient.

$$D_L = \alpha_L \times V_y' + D_M \quad (3)$$

where D_L , α_L , V_y' , and D_M are longitudinal dispersion coefficient, longitudinal dispersivity, real pore velocity and molecular diffusion coefficient, respectively. The hydrogeology and pollutant characteristics of the contaminated site are presented in **Table 1**.

2.2 Concept of mathematical model

The general governing equations describing the fate and transport of aqueous-phase and solid-phase species, respectively, in multi-dimensional saturated porous media ¹⁰⁾ are represented as:

$$\frac{\partial}{\partial t}(C_k) = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial(C_k)}{\partial x_j} \right] - \frac{\partial}{\partial x_i} (V'_i C_k) + \frac{q_s}{\theta} C'_k \pm r_k, \quad k = 1, 2, \dots, m \quad (4)$$

$$\frac{\partial \tilde{C}_k}{\partial t} = \mp r, \quad k = 1, 2, \dots, m \quad (5)$$

where m is the total number of species, 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}), D_{ij} is the hydrodynamic dispersion coefficient (L^2T^{-1}), V'_i is the pore velocity (LT^{-1}), q_s is the volumetric flux of water per unit volume of aquifer that represents source and sink (T^{-1}), C'_i is the concentration of source /sink (ML^{-3}), r_k represents all aqueous-phase reaction rate terms that describe the mass of the species removed or produced per unit volume per unit time ($\text{ML}^{-3} \text{T}^{-1}$), and θ is porosity. The real pore velocity can be obtained by dividing the saturated velocity by the porosity.

Contaminant transport model developed in this study represents the transport and the fate of the only aqueous phase of chlorinated organic compounds in the vertical direction. Thus the transformation of the aqueous phase of those species from the measured concentration (sorbed-phase concentration) was necessary. The following equilibrium equation is applicable.

$$C_k = \tilde{C}_k (1 - \theta) \times \frac{\rho_{solid}}{\theta} \quad (6)$$

where ρ_{solid} is soil density (ML^{-3}).

In general, chemical, physical and electrostatic interactions may contribute to the sorption of organic pollutants in soil and sediment. Sorption of hydrophobic compounds in soils can be attributed to the soil organic matter content ¹²⁾. Retardation factor using linear sorption isotherm was then applied to account for the delay of transportation of contaminants due to sorption into soil or sediment as follows

$$\tilde{C}_k = Kd_k \cdot C_k \quad (7)$$

$$R_k = 1 + Kd_k \left(\frac{\rho_b}{\theta} \right) \quad (8)$$

$$Kd_k = K_{oc,k} \cdot F_{oc} \quad (9)$$

$$\log K_{oc,k} = \log K_{ow,k} - 0.35 \quad (10)$$

where R_k , Kd_k , $K_{oc,k}$, $K_{ow,k}$, ρ_b , 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 bulk density of the sediment (i.e. the ratio of mass of dried soil to total volume of the soil in ML^{-3}) and the fraction of organic carbon, respectively ¹³⁾. $K_{oc,k}$ is relatively invariant for natural sorbents, and can be estimated from other physical properties of pollutants such as aqueous solubility or octanol/water partition coefficients.

Table 1 Hydrogeology and pollutant characteristics of the site.

Parameters	Unit	Layer 1	Layer 2
Dominating Material		Silty clay	Sand
Depth (L)	cm	230	370
Density of dioxins (ρ_{diox})	g/cm ³	1.827	1.827
Density of chlorobenzene (ρ_{cb})	g/cm ³	1.2	1.2
Density of water (ρ_{water})	g/cm ³	1.00	1.00
Porosity (θ)	-	0.2	0.15
Saturated Permeability (K_{sat})	cm/sec	10 ⁻⁵	10 ⁻³
Darcy velocity (V_y) for dioxin transport	cm/sec	18.3E-05	18.3E-03
Darcy velocity (V_y) for chlorobenzene transport	cm/sec	1.2E-06	1.20E-03
Pore velocity for (V'_y) for dioxin transport	cm/sec	9.14E-05	1.22E-02
Pore velocity for (V'_y) for chlorobenzene transport	cm/sec	6.0E-05	8.0E-03
Grain size	cm	5.0E-04	9.0E-03
Molecular diffusion coefficient (D_M)	cm ² /sec	1.0E-05	1.0E-05
Longitudinal dispersivity (α_L)	cm	5.0E-04	9.0E-03
Longitudinal dispersion coefficient (D_L) for dioxin transport	cm ² /sec	1.0E-05	1.2E-04
Longitudinal dispersion coefficient (D_L) for chlorobenzene transport	cm ² /sec	1.00E-05	8.2E-05
Soil density (ρ_{soil})	g/cm ³	2.643	2.645
Bulk density (ρ_b)	g/cm ³	2.115	2.5
Fraction of organic carbon content (F_{oc})	%	0.24 – 0.70	0.16

2.3 Mathematical model of dioxin transports

Essaid et al. (1995) summarized the existing models of transport and biodegradation. These models differ in dimensionality; representation of biological growth and contaminant degradation, and the number of processes simulated¹⁴. Most are limited to specific biodegradation processes that include a maximum of two substrates (carbon sources) and two electron acceptors. Some models include the transport and uptake of substances necessary for microbial growth (for example nitrogen and phosphorous).

Because of their high hydrophobicity dioxins tend to accumulate in biota and in sediment, which acts as a sink for these compounds. Depending on the amount of chlorines and substitution pattern, their sediment/water partition coefficient ranges from 10⁵ – 10¹²¹⁵. Furthermore Chapelle (1993) suggested that highly chlorinated molecules are resistant to aerobic oxidation but are subject to reductive dehalogenation, meanwhile lightly chlorinated molecules are resistant to anaerobic (reductive dehalogenation) but are subject to aerobic oxidation¹⁶. Similarly Andrieans et al (1994) stated that the only known biological process leading to a transformation of the highly chlorinated congeners under anaerobic condition is the microbial mediated reductive dechlorination observed in microcosms or mixed cultures¹⁷.

Five species of dioxin homologues transported in groundwater was considered as the first simulation scenario. Particularly biodegradation through dechlorination of higher chlorinated homologues to the lower ones was incorporated in this simulation. In addition this simulation coupled as well the last three dioxin homologues referred to as the dechlorination by products.

Table 2 Reaction parameters of dioxins.

Dioxin homologues	Octanol-Water Partitioning Coefficient (Mackay et al, 1992) ¹⁸⁾	First order degradation rate (Kjeller & Rappe, 1995) ¹⁹⁾	Molecular weight
	Log K_{ow}	Second ⁻¹	
OCDD	7.81	2.26779E-10	459.8
HeCDD	7.61	3.56157E-10	425.3
HxCDD	7.41	3.56157E-10	390.9
PeCDD	7.01	1.99772E-10	356.4
TeCDD	6.41	3.37038E-10	322
TrCDD	5.6	5.49372E-09	287.5
DCDD	5.4	1.09874E-08	253.1
MCDD	5	2.19749E-08	218.6

The partial differential governing equation expressing the transport and biotransformation of dioxins was presented below in which the anaerobic reductive dehalogenation/dechlorination was applied using sequential decay reaction⁶⁾.

$$R_O \frac{\partial}{\partial t} \{(OCDD)\} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial (OCDD)}{\partial x_j} \right] - \frac{\partial}{\partial x_i} \{V'_i (OCDD)\} - K_O (OCDD) \quad (11)$$

$$R_{He} \frac{\partial}{\partial t} \{(HeCDD)\} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial (HeCDD)}{\partial x_j} \right] - \frac{\partial}{\partial x_i} \{V'_i (HeCDD)\} + Y_{He/O} K_O (OCDD) - K_{He} (HeCDD) \quad (12)$$

$$R_{Hx} \frac{\partial}{\partial t} \{(HxCDD)\} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial (HxCDD)}{\partial x_j} \right] - \frac{\partial}{\partial x_i} \{V'_i (HxCDD)\} + Y_{Hx/He} K_{He} (HeCDD) - K_{Hx} (HxCDD) \quad (13)$$

$$R_{Pe} \frac{\partial}{\partial t} \{(PeCDD)\} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial (PeCDD)}{\partial x_j} \right] - \frac{\partial}{\partial x_i} \{V'_i (PeCDD)\} + Y_{Pe/Hx} K_{Hx} (HxCDD) - K_{Pe} (PeCDD) \quad (14)$$

$$R_{Te} \frac{\partial}{\partial t} \{(TeCDD)\} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial (TeCDD)}{\partial x_j} \right] - \frac{\partial}{\partial x_i} \{V'_i (TeCDD)\} + Y_{Te/Pe} K_{Pe} (PeCDD) - K_{Te} (TeCDD) \quad (15)$$

$$R_{Tr} \frac{\partial}{\partial t} \{(TrCDD)\} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial (TrCDD)}{\partial x_j} \right] - \frac{\partial}{\partial x_i} \{V'_i (TrCDD)\} + Y_{Tr/Te} K_{Te} (TeCDD) - K_{Tr} (TrCDD) \quad (16)$$

$$R_D \frac{\partial}{\partial t} \{(DCDD)\} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial (DCDD)}{\partial x_j} \right] - \frac{\partial}{\partial x_i} \{V'_i (DCDD)\} + Y_{D/Tr} K_{Tr} (TrCDD) - K_D (DCDD) \quad (17)$$

$$R_M \frac{\partial}{\partial t} \{(MCDD)\} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial (MCDD)}{\partial x_j} \right] - \frac{\partial}{\partial x_i} \{V'_i (MCDD)\} + Y_{M/D} K_D (DCDD) - K_M (MCDD) \quad (18)$$

where $OCDD$, $HeCDD$, $HxCDD$, $PeCDD$, $TeCDD$, $TrCDD$, DCD , $MCDD$ represent contaminant concentrations of various species (ML^{-3}); K_O , K_{He} , K_{Hx} , K_{Pe} , K_{Te} , K_{Tr} , K_D and K_M are first-order anaerobic degradation rate constants (day^{-1}); and R_O , R_{He} , R_{Hx} , R_{Pe} , R_{Te} , R_{Tr} , R_D and R_M are retardation factors. Stoichiometric yield values, Y , can be calculated from the reaction stoichiometry and molecular weights by which the molecular weight of the daughter compounds

are divided by the molecular weight of the parent compounds.

The reaction parameters of dioxins comprising octanol-organic carbon partitioning coefficient, sorption rate and first order degradation rate are given in **Table 2**.

2.4 Mathematical model of chlorobenzene transport

Due to its extremely high hydrophobicity, theoretically dioxin transport in groundwater is hard to occur. If they were able to move, nevertheless, the different solubility among five dioxin homologues may cause the lower chlorinated dioxin homologues concentration increase with depth, whereas most of higher chlorinated dioxin homologue may adsorbed onto soil material instead of moving downward. It may result in the accumulation of the lower chlorinated dioxin concentration at the deeper site. Thus the higher one concentration may decrease with depth. However, based on the measured data, both the higher and lower chlorinated dioxin homologue indicate the same vertical transport profile pattern. Therefore the existence of a solvent is likely to be reasonable to bring dioxins downward. Furthermore it is supported as well by the measured data indicating that dioxins and a solvent (i.e. chlorobenzene) have a positive correlation. Since dioxins and chlorobenzene are non polar chemical compounds, it seems likely that some types of chlorobenzene (e.g. 0-dichlorobenzene and mono-dichlorobenzene) are able to dissolve dioxins at the considerably amount of concentration. Based on the facts mentioned above, thus the chlorobenzene transport simulation in groundwater was carried out as the second simulation scenario.

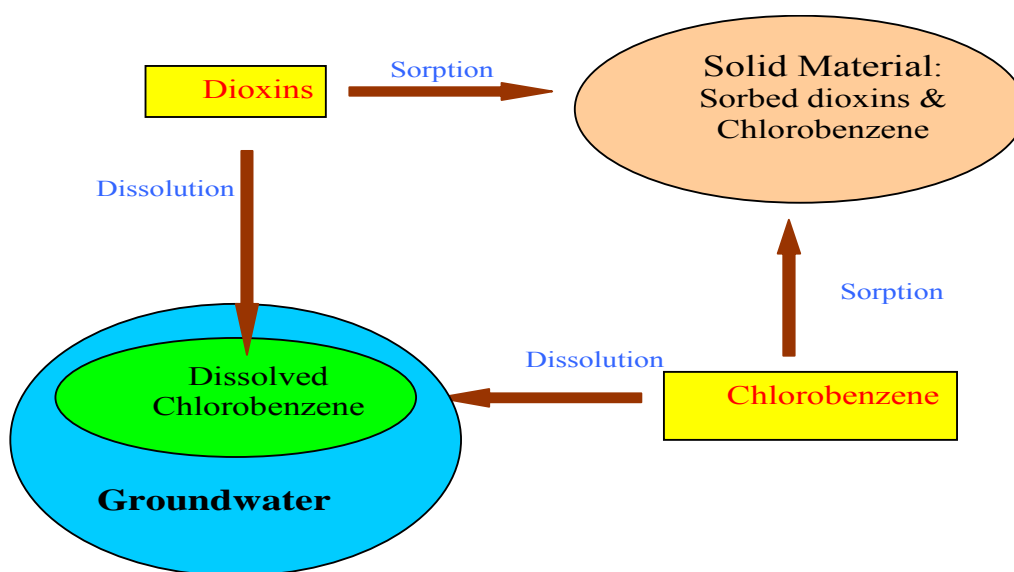


Fig.2 Schematization of contamination process.

Chlorobenzene classified as DNAPL (dense non-aqueous phase liquid) has high density, moderate solubility and low viscosity. Even though a various phases of DNAPL were commonly found in the subsurface environment, the aqueous phase of chlorobenzene was a sole phase considered in this study. In this second scenario chlorobenzene transport which comprises

advection, dispersion, and sorption processes occurring simultaneously was simulated applying the following equation

$$R_{CB} \frac{\partial(C_{CB})}{\partial t} = \frac{\partial}{\partial x_i} \left[D_{ij} \frac{\partial(C_{CB})}{\partial x_j} \right] - \frac{\partial}{\partial x_i} (V'_i C_{CB}) \quad (19)$$

where C_{CB} is the aqueous-phase concentration of chlorobenzene (ML^{-3}), and R_{CB} is retardation factor of chlorobenzene. This assumes that dioxins concentration profiles can be obtained after the concentration of C_{CB} in aqueous and solid phases are calculated by using Eq.19. Whereas the retardation factor of chlorobenzene can be gained by using Eq. 7-10. Hence the contamination process involving those mentioned processes above is illustrated in **Fig.2**.

3. Modeling Methodology

The one dimensional solute transport model was proposed to recreate the vertical transport and fate of multi-species of chlorinated organic compounds as a result of the processes of advection, dispersion, and reaction in porous media. The numerical solution, model design, calibration and sensitivity analysis employed in this modeling are described in the following sections.

3.1 Numerical solution

These pollutant transport and fate simulated using the so- called Method of Characteristic (MOC) through splitting up the advection-dispersion equation into two components: an advection component is solved by means of a particle tracking technique and a dispersion component is solved by the finite different method. Normally MOC is used to eliminate numerical dispersions that are encountered when applying the finite different method to advection-dominated problem²⁰⁾.

In the original MOC code one set of particles was used to simulate transport of a single solute species⁴⁾. Variations of the MOC model was developed that handle two concentrations per particle and two particles set with a single concentration each. In modified version of the MOC code is referred to as BIOMOC the MOC model was expanded to handle multiple particle sets, each particle having multiple solute species concentrations associated with it³⁾. This approach allows solute species having similar sorption characteristics to be represented by a single particle set.

In this study the advection-dispersion MOC code (Jinno, 2001) constructed using **FORTTRAN 6.0** was modified to simulate multi species of dioxin transports in groundwater and chlorobenzene transport in groundwater representing the transport of chlorinated organic pollutants present in the groundwater system of interest²¹⁾. In the first scenario, the eight particle set was introduced in which each of them carried a dioxin homologue with each velocity and each retardation factor.

The MOC numerical code performed in this study can be described as follows. Initially, particles of each set are distributed uniformly throughout the finite-difference grid. During a time step increment, each particle is moved based on the average velocity at the particle location. Due to each species sorption rate, the retarded velocity is used. After all the particles have been moved, an average concentration for each grid is calculated based on the average of the concentrations of the particles located within the grids. This new concentration is the result of advection transport only. Explicit finite-difference approximations are then used to solve for the change in concentration due to dispersion using the average of the concentration from the previous time step and the advection concentration. In the case of dioxin transport, the degradation of dioxins is then incorporated using a sequential decay reaction. Calculation of this degradation term uses the average of the

concentration as well. After summing up the change of concentration due to dispersion and degradation processes then the arrangement of the returning particles were undertaken. Finally the increased concentration is used for updating the concentration of further grids. This MOC steps can be also seen in **Fig.3**.

3.2 Model design

The concept of the mathematical model is transformed to a form suitable for numerical modeling. Essink (2001) suggested that this step in the modeling protocol includes the design of the domain partition, the selection of the length of the time steps (when transient), the setting of the boundary and initial conditions, and the selection of system parameters and hydrologic variables²². Model design applied in this study is shown in **Table 3**.

Number of grid	61
Distance between grid	10 cm
Time increment	10000 seconds
Simulation period	50 years
Boundary Condition	- Mass flux at the top - Concentration gradient is equal to zero ($\partial C/\partial y = 0$) at the bottom
Initial condition	No background pollutant concentration

3.3 Calibration

Calibration is adjusting parameters aiming to demonstrate that the model is capable of producing output matching the value of measured data. Procedure for calibrating applied in this study is by manual trial and error selection of parameters which included mass flux rate, mass flux period and F_{oc} as the preliminary test demonstrated that these three parameters were the main influential parameters.

3.4 Sensitivity analysis

The purpose of a sensitivity analysis is quantify the uncertainty in the estimates of model parameter on calibrated model result which is typically preformed by changing the value of one parameter at a time. Particularly the result of this analysis is expressed as the effects of the parameter change on the spatial distribution of concentration. In this study the sensitivity analysis was undertaken by observing the behavior of the concentration profile as a given parameter was changed.

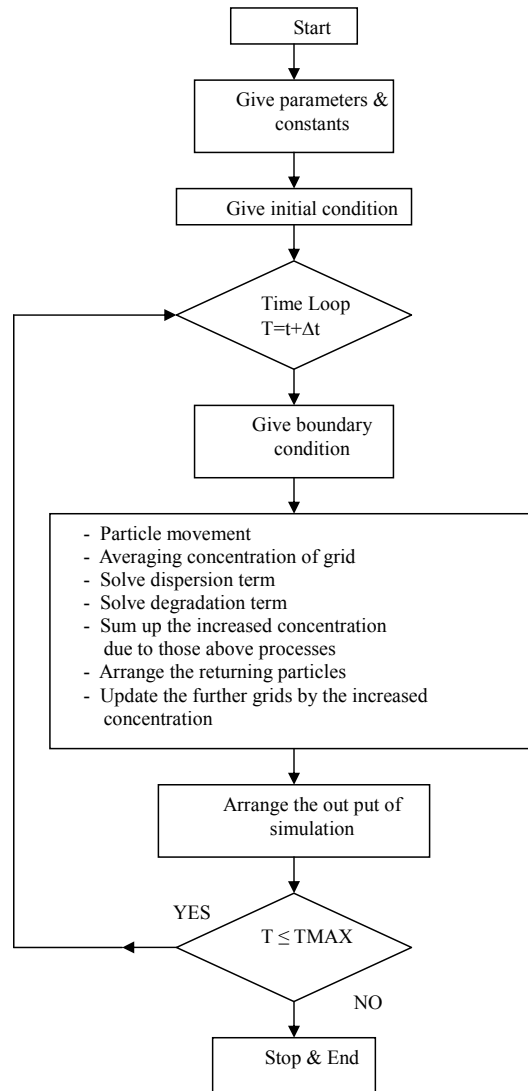


Fig.3 Numerical simulation applying MOC.

4. Result and Discussion

The model simulation result of the first scenario in which eight species dioxins were transported in groundwater indicated that there was no significant concentration in the model domain after 50 years of simulation. The high rate of sorption into solid material due to high hydrophobicity of the dioxins (K_{oc}) and high content of organic carbon of material (F_{oc}) particularly in the silty clay layer are likely to retard them to mobilize further downward. It can be noted that the retardation factor of 1.56×10^4 of the highest chlorinated dioxin homologue (OCDDs) and 622.0 of the lowest chlorinated dioxin homologues (TeCDDs) were used based on the F_{oc} measurement. In addition, biotransformation from higher chlorinated dioxins to lower chlorinated dioxins seems unlikely to take place probably as a result of their extremely low degradation rate.

The second simulation scenario was performed assuming that the transport of chlorobenzene in groundwater can transport the whole species of contaminants. The mass flux magnitude and mass flux period based simulation scenarios are illustrated in **Fig.4**. The developed model was calibrated applying 23 cases by which various F_{oc} , mass flux magnitude and mass flux period were given (see **Table 4**). The simulation result applying those cases can be summarized into four distinctive results which are described as follows; The first result demonstrated that the pollutant concentration might change slightly as the different order of mass flux magnitudes was released using transport time of 50 years, F_{oc} of 0.24 % and mass flux period of 25 years as depicted in **Fig.5**. Similarly, the second result applying transport time of 50 years, F_{oc} of 0.24% and mass flux rate of 1.0×10^{-6} mg/(cm² sec), revealed that the change of pollutant concentration resulting from the shift of mass discharge period were profound as shown in **Fig.6**. Furthermore, **Fig.7** shows the third result in which the change of concentration profile was obviously seen as the different F_{oc} was given. This simulation case employed transport time of 50 years, mass flux period of 25 years and mass flux rate of 1.0×10^{-6} mg/(cm² sec). Meanwhile the change of profile behavior can not be found as the change of max flux magnitude and mass flux period were provided. In contrast this change appeared significantly as various F_{oc} was applied.

Nevertheless, the developed model disregarded the impact of pumping conducted to remedy the contaminated area whose the profile of pollutant concentration should be affected. It probably reasoned the high of root mean square error (RMSE) of the calibrated model (see also **Table 3**). Moreover the pumping most likely resulted in the sudden decrease of contaminant concentration at the slightly upper and middle part. Therefore the fourth result of simulation which applied F_{oc} ranging approximately from 0.5 to 0.6 %, mass flux period of 25 years and mass flux rate of 1.0×10^{-6} mg/(cm² sec) seems to be appropriate as given in **Fig.7**. Referring to the last result, it then can be considerably realistic to estimate that as much as 1.0×10^{-6} mg/(cm² sec) of mass flux magnitude of chlorobenzene was continuously discharged to the groundwater systems of the contaminated site for 25 years from 1950 to 1975. The profile of chlorobenzene concentration with different applying time under the three given parameters of the last result is presented in **Fig.8**.

In addition the distinctly different behavior of pollutant concentration profile influenced by the extremely different magnitude order of apparent velocity between the first layer (0 – 230 cm) and the second layer (230 – 600 cm) could be well demonstrated by the model. Accordingly the accumulation of pollutant concentration in the lower part of the model domain was observed. It was probably due to the fact that an impermeable layer beneath the second layer impeded the pollutant to migrate more downward.

The sensitivity analysis was carried out in this study of which F_{oc} , mass flux rate and mass flux period were used to evaluate the effect of these parameter changes on the distribution of concentration. By examining the behaviors of the four simulation results it was proved that the most sensitive parameter was F_{oc} , whereas mass discharge period and the change of mass flux rate moderately influenced the pollutant distribution concentration. As a result of the limited available measured data, however, the model verification using other set of data could not be performed.

The developed model can be useful to carry out a preliminary prediction of vertically pollutant distribution and fate spatially and temporally which is a crucial tool in a proper monitoring design. Several efforts must be planned to improve the reliability of this model in order to be effectively applied for evaluation of either natural attenuation or man induced processes.

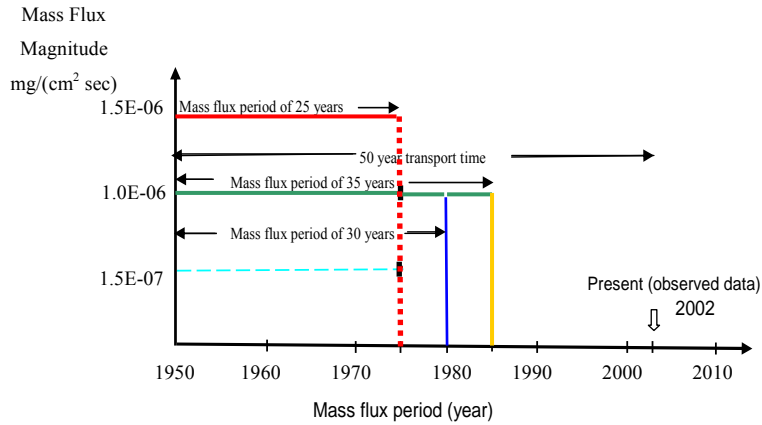


Fig.4 Schematization of mass flux based.

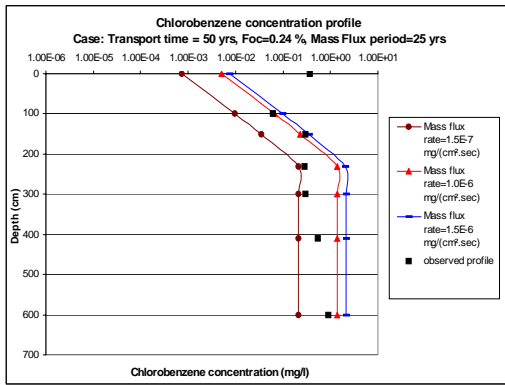


Fig.5 Chlorobenzene concentration profile with different mass flux rates.

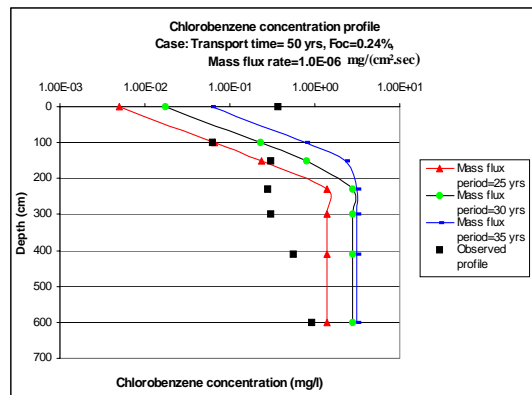


Fig.6 Chlorobenzene concentration profile with different mass flux periods.

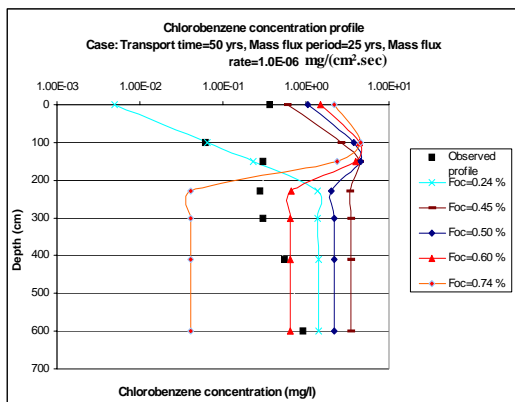


Fig.7 Chlorobenzene concentration profile with different F_{oc} .

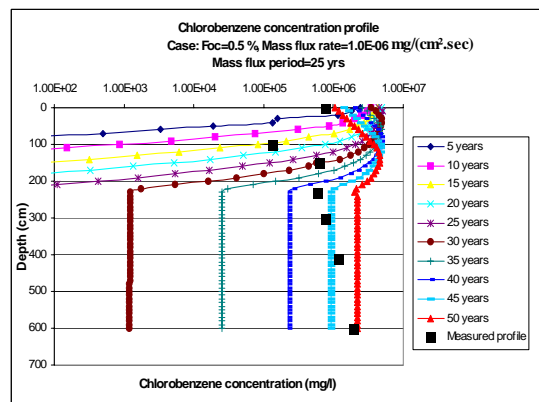


Fig.8 Chlorobenzene concentration profile with different transport times.

Table 4. Calibrated simulation parameters.

Case	F_{oc} (%)	Mass flux Magnitude mg/(cm ² sec)	Mass flux Period (years)	Transport Time (years)	Standard Deviation	RMSE
1	0.24	1.50E-07	25	50	0.71	0.84
2	0.24	1.50E-07	30	50	0.52	0.72
3	0.24	1.50E-07	35	50	0.46	0.68
4	0.24	1.00E-06	25	50	0.325	0.57
5	0.24	1.00E-06	30	50	1.98	1.41
6	0.24	1.00E-06	35	50	3	1.73
7	0.24	1.50E-06	25	50	0.86	0.93
8	0.24	1.50E-06	30	50	5.97	2.44
9	0.24	1.50E-06	35	50	8.73	2.95
11	0.74	2.50E-06	25	50	26.57	5.15
12	0.74	1.00E-06	25	50	4.37	2.09
13	0.74	2.50E-06	20	50	19.565	4.42
14	0.74	5.00E-06	25	50	109.07	10.44
15	0.74	3.50E-06	20	50	38.8	6.23
16	0.74	5.00E-06	20	50	80.29	8.96
17	0.4	2.50E-06	20	50	81.36	9.02
18	0.34	2.50E-06	25	50	319.18	17.87
19	0.44	3.00E-06	25	50	82.84	9.10
20	0.4	1.00E-06	25	50	6.67	2.58
21	0.45	1.00E-06	25	50	6.97	2.64
22	0.6	1.00E-06	25	50	4.83	2.20
23	0.5	1.00E-06	25	50	4.93	2.22

5. Conclusion

The dechlorination of the highest chlorinated dioxins (OCDDs) associated with increasing concentration of the lower chlorinated dioxins, and the production of the dechlorinated by products can not be represented by the model, due to dioxin high sorption rate and low degradation rate.

In addition the second simulation scenario results demonstrated that the developed model can be used to make a preliminary prediction of mass flux magnitude of the pollutants and the time period of their discharge. It can be noticed as well that the profile concentration of chlorobenzene was affected by F_{oc} , mass discharge period and mass flux rate.

Furthermore the difference in profile concentration behavior of the pollutant due to distinctly different material type and the accumulation of concentration at the lower part of contaminated site can be recreated by the developed model.

The sensitivity analysis revealed that F_{oc} was the most sensitive parameter, whereas mass discharge time period and mass flux rate showed approximately similar sensitivity toward the distribution of concentration.

The developed model, however, disregarded the effect of pumping efforts. Therefore extension of the model should be planned in order to be able to incorporate the more realistic natural attenuation of the present contaminants as well as a probable man induced processes.

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References

- 1) USEPA, *The Inventory of Sources of Dioxin in the United States*. Office of Research and Development, EPA/600/P-98/002Aa, External Review Draft, April (1998).
- 2) Mitsui Chemical, Inc, *Responsible Care Report*. http://www.mitsui-chem.co.jp/e/rc/pdf/rc03_e.pdf, pp 18 (2003).
- 3) Essaid, H.I., Bekins, B.A., *A Multispecies Solute-Transport Model with Biodegradation*. Water-Resources investigation Report pp.97-4022. U.S.G.S, (1997).
- 4) Konikow, L.F., and Bredehoeft, J.D., *Computer model of two-dimensional solute transport and dispersion in groundwater*: U.S.GS, Techniques of Water-Resources Investigation, Book 7, Chap.C2. p.90 (1978).
- 5) Rifai, S.H., Bedient, P.B., Borden, R.C., Haasbeek, J.P., *BIOPLUME II Computer model of two-dimensional contaminant transport under the influence of oxygen limited biodegradation in groundwater*, National Center for Groundwater Research, Roce University. p.5 (1987).
- 6) Clement, T.P., RT3D- *A modular computer code for simulating reactive multi-species transport in 3-dimensional groundwater aquifers*, Pacific Northwest National Laboratory Report, PNNL-11720. <http://bioprocess.pnl.gov/rt3d.htm>. pp.31-32 (1997).
- 7) Clement, T.P., Sun, Y., Hooker, B.S., Petersen, J.N., *Modeling multi-species reactive transport in groundwater aquifers*. Ground Water Monit. Rem. 18 (2), pp.79-92 (1998).
- 8) Bear J. and Verruijt, *Modeling Groundwater Flow and Pollution*. D. Reidel Publishing Company, Dodrecht, Holland. p.13 (1997).
- 9) Bredehoeft, J., 2005. *The conceptualization model problem-surprise*. Hydrogeology Journal Vol.13, No. 1, March 2005. pp.37-46.
- 10) Clement, T.P, Johnson , C.D., Sun, Y., Klecka, G.M., Bartlett, C., *Natural attenuation of chlorinated ethane compounds: model development and field-scale application at the Dover site*. Journal of Contaminant Hydrology 42 pp.113-140 (2000).
- 11) Bear, J., *Dynamics of fluids in Porous media*. American Elsevier. New York, p.764 (1972).
- 12) Grathwohl, P., *Diffusion in Natural Porous Media; Contaminant Transport, Sorption/Desorption and Dissolution Kinetics*. Kluwer Academic Publishers, Massachusetts. U.S.A. p.16 (1998).
- 13) Appelo, C.A.J., and Postma, D., *Geochemistry, groundwater and pollution*. A.A. Balkema, Rotterdam, Holland, p.343 (1994).
- 14) Essaid, H.I., Bekins, B.A., Godsy, E.M., Warrant, E., Baedecker, M.J., Cozzarelli, I.M., *Simulation of aerobic and anaerobic biodegradation processes at a crude oil spill site*. Water Resour. Res.31 (12), pp.3309-3327 (1995).
- 15) Merel Toussaint, Rene Van Herwijnen and John R Parsons, *Anaerobic Bacterial Dehalogenation of Polyhalogenated Dioxins and Furans*. In: Rolf-Michael Wittich, (ed): *Biodegradation of dioxins and furans*. Springer-Verlag Berlin Heidelberg and R.G. Landes Company, TX, USA, pp.29-52 (1998).
- 16) Chapelle, F.H., *Groundwater Microbiology & Geochemistry*. John Wiley & Son, Inc. New York, U.S.A. p.374 (1993).

- 17) Andriaens, P., Fu, Q. & Grbic-Galic, D., *Bioavailability and transformation of highly chlorinated dibenzo-p-dioxins and dibenzofurans in anaerobic soils and sediments*. Environ.Sci.Technol.29, pp.2252-2260 (1995).
- 18) Mackay, D., Shiu, Y., and Ma, K.C., *Illustrated Handbook of Physical-Chemical Properties and Environmental fate for Organic Chemicals*, Vol.2. Lewis Publishers, Chelsea, Mich. p.595 (1992).
- 19) Kjeller LO, Rappe C., *Time trend levels, patterns and profiles for polychlorinated dibenzo-p-dioxins, dibenzofurans and biphenyls in a sediment core from the Baltic proper*. Environ. Sci. Technol, 29 pp.346-355 (1995).
- 20) Zheng, Z. and Bennet, GD., *Applied Contaminant Transport: Modeling, Theory and Practice*, Van Nostrand Reinhold, New York. p.74 (1995).
- 21) Kenji Jinno, *Transport Numerical Analysis in Groundwater*. Kyushu University Press, Japan. p.34-39 (2001), (in Japanese).
- 22) Essink Oude., G.H.P., *Groundwater Modeling*. Lecture Note L 4018/GWM I. Departement of Geophysics, Institute of Earth Sciences. Interfaculty of Hydrology Utrecht. Utrecht University, the Netherlands. p.46 (2000).