Study Project

Tracer Transport in Cohesive Soils and Related Risk Assessment for Different Herbicides

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Date: 24-December-2017

Content

1 Introduction

Herbicides are inherently toxic to certain plants, so they are effective tools to kill or suppress undesired plant species by interfering with important plant processes such as photosynthesis. Nevertheless, environmental water and soil can be easily exposed and contaminated by herbicides during and after application. "If we are going to live so intimately with these chemicals eating and drinking them, taking them into the very marrow of our bones - we had better know something about their nature and their power [Rachel Carson, 1962, Silent Spring] ". Therefore, understanding the transport and transformation processes of herbicides is essential to assess related risks and avoid unexpected environmental damages.

In this study project, the transport behavior was modeled for two typical soils, Calcaric Regosol and Luvisol, whose tracer distributions, as well as soil hydraulic parameters after van Genuchten (1980) and Mualem (1976) were provided in the Excel sheet "irrigation_experiments.xls". In addition, mobility and persistence of two herbicides, Simazine and Atrazine, were analyzed in target soils.

2 Theory and methods

In this report, the transport and transformation behaviors of contaminants in selected soils were characterized by advection, dispersion, adsorption, desorption and degradation processes. Simulation and modeling were accomplished by MATLAB.

2.1 Advection and dispersion

Advection refers to the transport of solutes by the bulk movement of fluid, specifically speaking, pollutants are simply carried by the bulk movement of the groundwater. Dispersion is the spreading or mixing phenomenon caused by the variability of the complex and microscopic velocities through the soil pores. Therefore, it is related to the heterogeneity present in the soil.

The basic advection-dispersion equation for transport in the soil can be described as:

$$\frac{\partial C_w}{\partial t} = -v_z \frac{\partial C_w}{\partial z} + \frac{\partial}{\partial z}\left(D_{is} \frac{\partial C_w}{\partial z} \right) \tag{2-1}$$

with

$$v_z = \frac{q_w}{\theta} \tag{2-2}$$

where C_w is the concentration in the water phase [kg/m³]

V_z is average transport velocity [m/s]

D_{is} is the dispersion coefficient [m²/s]

q_w is the Darcy flow [m/s]

θ is the soil water content [m³/m³]

z is the depth [m]

1) Darcy flow q_w

Based on Darcy's Law, which is developed for saturated flow in porous media, Richard equation, a nonlinear partial differential equation, describes the movement of water in unsaturated soils.

$$q = -k(\theta)\frac{\partial \varphi_{hydr}}{\partial z} \qquad (2\text{-}3)$$

$$\varphi_{hydr} = \varphi_{matric} + \varphi_z \qquad (2\text{-}4)$$

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left(k(\theta)\frac{\partial \varphi_{hydr}}{\partial z}\right) \qquad (2\text{-}5)$$

where k is hydraulic conductivity [m/s]

φ_{hydr} is hydraulic potential [m]

φ_{matric} is matric potential [m]

φ_z is gravitational potential [m]

2) Soil water content θ

The amount of water remaining in the soil is called soil water content or soil moisture. Its relation with hydraulic conductivity is shown as below:

$$S = \frac{\theta - \theta_r}{\theta_s - \theta_r} \qquad (2\text{-}6)$$

$$k(S) = k_s S^{0.5}\left[1 - (1 - S^{1/m})^m\right]^2 \qquad (2\text{-}7)$$

$$m = 1 - \frac{1}{n} \qquad (2\text{-}8)$$

where S is relative saturation [-]

θ is soil water content [m³/m³]

θ_r is residual soil water content [m³/m³]

θ_s is saturated soil water content [m³/m³]

k_s is saturated hydraulic conductivity [m/s]

n is the width of the pore size distribution [-]

In this project, soil hydraulic conductivity k and dispersion coefficient D_{is} were not given, so they relied on experiment works and D_{is} of two different soils were determined by the method of moments.

2.2 Adsorption and desorption

Adsorption and desorption are the major actions that affect the mobility of pollutants in soils and sediments. Briefly speaking, when herbicides are applied into soils, parts of them will be absorbed to the soil particles while others remain in the water phase. These processes can be expressed as:

$$C_s = \frac{k_{ad}}{k_{des}} C_w \qquad (2\text{-}9)$$

or
$$\frac{\partial C_s}{\partial t} = k_{ad} C_w - k_{des} C_s \qquad (2\text{-}10)$$

where C_s is the concentration of solute in the solid phase [kg/kg]

C_w is the concentration of solute in the water phase [kg/m³]

k_{ad} is adsorption coefficient [m³/(kg*s)]

k_{des} is desorption coefficient [1/s]

Assuming a constant soil moisture and a constant water flux, the general mass balance can be given by:

$$\frac{\partial(\theta C_w + \rho C_s)}{\partial t} = \frac{\partial(q_w C_w)}{\partial z} + \frac{\partial}{\partial z}(D \frac{\partial C_w}{\partial z}) \qquad (2\text{-}11)$$

$$\frac{\partial C_w}{\partial t} + \frac{\rho d C_s}{\theta d C_w} \frac{\partial C_w}{\partial t} = -v_z \frac{\partial C_w}{\partial z} + \frac{\partial}{\partial z}(D_e \frac{\partial C_w}{\partial z}) \qquad (2\text{-}12)$$

with
$$D_e = \frac{D}{\theta} \qquad (2\text{-}13)$$

where D is the desorption coefficient [m²/s]

D_e is the effective desorption coefficient [m²/s]

To simplify the equation 2-12, a retardation coefficient R can be deduced as:

$$R \frac{\partial C_w}{\partial t} = -v_z \frac{\partial C_w}{\partial z} + \frac{\partial}{\partial z}(D_e \frac{\partial C_w}{\partial z}) \qquad (2\text{-}14)$$

6

with
$$R = 1 + \frac{\rho dC_s}{\theta dC_w}$$
(2-15)

R is greater or equal to 1. To determine the retardation coefficient in an equilibrium adsorption condition, there are linear and non-linear cases that will be introduced below.

2.2.1 Linear case

In the linear case where C_s and C_w vary linearly with each other, the retardation coefficient R is a constant.

$$R = 1 + \frac{\rho K_d}{\theta}$$
(2-16)

$$K_d = \frac{C_s}{C_w} = \frac{k_{ad}}{k_{des}} = \text{const.}$$
(2-17)

where K_d is the distribution coefficient, representing the slope of the isotherm [-]

In this case, the equation 2-14 becomes similar to the advection-dispersion equation 2-1, while with the average transport velocity v_z and dispersion coefficient D_{is} divided by R as presented below:

$$\frac{\partial C_w}{\partial t} = -\frac{v_z}{R} \frac{\partial C_w}{\partial z} + \frac{\partial}{dz} \left(\frac{D_{is}}{R} \frac{\partial C_w}{\partial z} \right)$$
(2-18)

If R>1, the average transport velocity v_z gets smaller, leading to pollutants retardation for better degradation.

2.2.2 Non-linear case

Nonetheless, the linear case is an ideal but not realistic situation. In the environment, non-linear case, where retardation coefficient R is a function of pollutants concentration in the water phase C_w, is more common.

There are basically two typical adsorption isotherms, the Langmuir adsorption isotherm and the Freundlich adsorption isotherm. In this project, Freundlich adsorption isotherm, which proposes the description of adsorption isotherm as a power function, was applied and can be expressed as follows:

$$C_s = K_f C_w^{\beta}$$
(2-19)

$$R(C_w) = 1 + \frac{\rho}{\theta} \frac{dC_s}{dC_w} = 1 + \frac{\rho}{\theta} K_f C_w^{\beta-1} \beta$$
(2-20)

where K_f is Freundlich coefficient [-]

β is the Freundlich exponent [-]

β corresponds to 1/n in the notation in <u>Footprint database from EU-Project</u>. It is a constant only valid for a certain concentration range and increases with decreasing concentration.

Fig.2.1 shows the comparison of three types of adsorption isotherms. The slope of Freundlich isotherm at low concentration is larger than that in higher concentration ranges, which means more adsorption and retardation occur at low concentration.
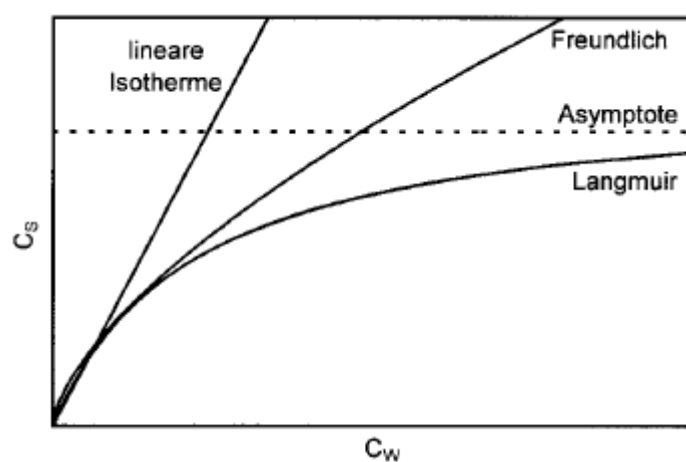

Fig.2.1 Comparison of 3 Adsorption Isotherms

2.3 Degradation/ decay

The mechanisms in former two sections discuss the transport of conservative solutes. In fact, the soil is a microbiological system, where microorganisms ingest or get closely associated with herbicides in order to degrade these molecules in either anaerobic ways like de-mineralization for protection of groundwater against NO_3^-, or aerobic ways such as metabolic and co-metabolic degradation.

Frehse and Anderson (1983) suggested that the rate of microbial metabolism of herbicides in soils was determined by three important elements: the availability, quantity, and the activity level of the chemicals or enzymes of the microorganisms to perform degradation. The system driving parameters are soil moisture, temperature, oxygen content, pH, and nutrient status of the soil, which are characterized by λ.

In this project, the degradation is assumed to be first order, with decay rate being proportional to the solute concentration in water phase as shown below:

$$dC_{\mathrm{w}} = -\lambda C_w dt \tag{2-21}$$

$$C_{\mathrm{w}}(t) = C_{\mathrm{w}0}e^{-\lambda t} \tag{2-22}$$

where $C_{\mathrm{w}0}$ is the initial solute concentration in water phase [kg/m³]

λ is the first order decay constant [-]

t is the time [s]

Hence, the equation 2-11 is extended as:

$$\frac{\partial(\theta C_w + \rho C_s)}{\partial t} = \frac{\partial(q_w C_w)}{\partial z} + \frac{\partial}{\partial z}(D\frac{\partial C_w}{\partial z}) - \lambda C_{\mathrm{w}} \tag{2-23}$$

2.4 Analytical model

Assuming a constant water flux and a soil moisture, linear adsorption isotherm, a first-order decay, the equation 2-14 becomes:

$$R\frac{\partial C_{\mathrm{w}}}{\partial t} = -v_z\frac{\partial C_{\mathrm{w}}}{\partial z} + \frac{\partial}{\partial z}(D_e\frac{\partial C_{\mathrm{w}}}{\partial z}) - \lambda C_{\mathrm{w}} \tag{2-24}$$

As R, v_z, D_e, λ are constant values, this equation has an analytical solution based on Gaussian distribution, given as:

$$\frac{\theta}{m_0}C_{\mathrm{w}}(z,t_c) = \frac{1}{\sqrt{4\pi\frac{D_e}{R}t_c}}\exp(-\frac{(z-\frac{v_z}{R}t_c)^2}{4\frac{D_e}{R}t_c})exp(-\lambda \mathrm{t}_c) \tag{2-25}$$

where m_0 is total applied solute mass [kg]

t_c is the total transport time, a constant [s]

The result of this model is a Gaussian shaped concentration curve with the center of mass traveling with the advection velocity.

2.5 The method of moments

The method of moments procedure utilizes tracer experiments in the field and measures the concentration as a function of depth at a fixed time to estimate advective transport behavior. It assumes that the concentration distribution follows the analytical solution as described in equation 2-25 but considering neither the retardation (R=1) nor the decay (λ=0).

From a concentration pattern $C_{\mathrm{n}}(x,z,t)$, the mean in the x-axis is taken and then normalized by the total mass m_0 to get a normalized concentration distribution:

$$C_{\mathrm{n}}(z_i) = \frac{C(z_i)}{m_0} \qquad (2\text{-}26)$$

1) The first moment represents the average transport distance $\bar{z}$ from the center of mass, estimated by:

$$\bar{z} = \sum_i z_i * C_{\mathrm{n}}(z_i) * V(z_i) \qquad (2\text{-}27)$$

where i is the grid number [-]

$\quad C_{\mathrm{n}}(z_i)$ is the normalized concentration [$1/m^3$]

$\quad V(z_i)$ is the volume of the grid cell [m^3]

The average velocity is then defined as:

$$\bar{v} = \frac{\bar{z}}{t} \qquad (2\text{-}28)$$

where t is the duration time of the experiment [s]

2) The second moment represents the variance from the mean transport distance and is given by:

$$\mathrm{var}(z_i) = \sum_i C_n(z_i) * V(z_i) * (z_i - \bar{z})^2 \qquad (2\text{-}29)$$

From this, the dispersion coefficient D_{is} and Peclet number Pe are calculated.

$$D_{\mathrm{is}} = \frac{\mathrm{var}(z_i)}{2t} \qquad (2\text{-}30)$$

$$Pe = \frac{(\bar{v})^2 t}{D_{\mathrm{is}}} \qquad (2\text{-}31)$$

where the Peclet number is defined as the ratio of the rate of advection of solutes by the flow to the rate of diffusion of the same solutes driven by an appropriate gradient.

2.6 Experiment

The database consists of a set of plot scale irrigation experiments with Bromide and the dye Brilliant Blue FFC that were conducted with an automated sprinkler.

One day after irrigation, two profiles were excavated regarding soil samples taken on two 10 cm*10 cm grids and analyzed for their Bromide concentration.

In this project, soils from sites Inf21 (Luvisol, topsoil) and Inf23 (Calcaric Regosol, topsoil) were analyzed.

3 Results

3.1 Task1 Transport behavior of typical soils in a rural catchment

3.1.1 Introduction of Calcaric Regosol and Luvisol

1) Calcaric Regosol

In the FAO World Reference Base for Soil Resources, Regosols are very weakly developed mineral soil in unconsolidated materials. Regosols are extensive in eroding lands, particularly in arid and semiarid areas and in mountain regions.

2) Luvisol

Luvisols are suitable for a wide range of agricultural uses due to the mixed mineralogy, high nutrient content, and good drainage properties. Luvisols form on flat or gently sloping landscapes under climatic regimes ranging from cool temperature to warm Mediterranean.

Luvisols are technically characterized by a surface accumulation of humus overlying an extensively leached layer that is nearly devoid of clay and iron-bearing minerals. Below the latter lies a layer of mixed clay accumulation that has high levels of available nutrient ions comprising calcium, magnesium, sodium or potassium.

3) Given soil data

Tab.1 Given Soil Data

Soil	Date	Land Use	ρ [kg/m³]	θ	θ_s	θ_r	α [1/m]	n	Ks [m/s]
Luvisol	7/96	wheat	1410	0.179	0.47	0.11	5.9	1.23	$5.00*10^{-6}$
Calc.Reg	7/96	corn	1300	0.159	0.44	0.06	0.4	2.06	$1.70*10^{-6}$

3.1.2 Concentration patterns

A) Select two different sites, visualize and compare the concentration patterns using both concentration patterns.

Selected sites are Inf21 and Inf23. Their log concentration and concentration profiles over depth are shown in Fig.3.1.

Since two concentration profiles were available for each site, their concentrations were averaged into one (see "cinf21.txt" and "cinf23.txt") before modeling.
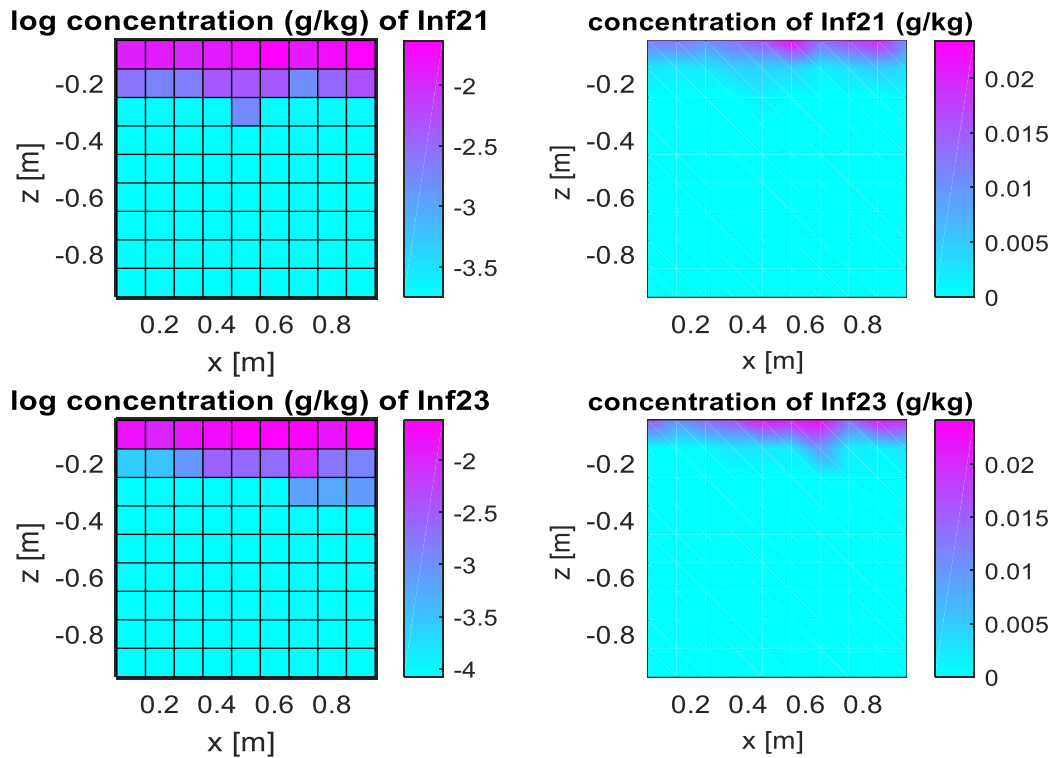

Fig.3.1 Log Concentration and Concentration Profile of Inf21 and Inf23

3.1.3 Average transport velocity and dispersion coefficient

B) Determine the average transport velocity $\bar{v}$ and the dispersion coefficient D_{is} using the method of moments for each site. Explain how you deal with the 2 profiles.

The average transport velocity $\bar{v}$, the dispersion coefficient D_{is}, Peclet number Pe and soil conductivity k of both sites are listed in Tab.2. Furthermore, normalized concentration and mass probabilities over depth of both sites were calculated and plotted as below:

Tab.2 Calculated Soil Data by Matlab

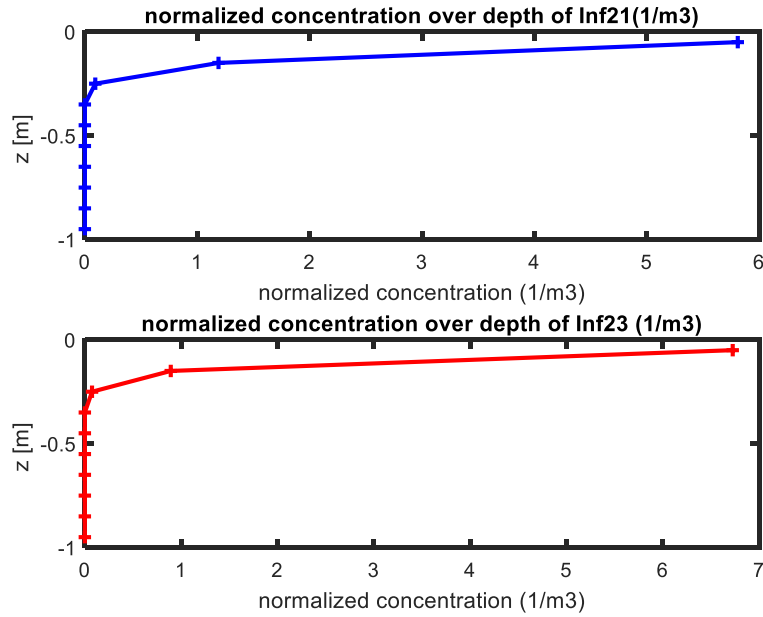| Site	$\bar{v}$ [m/s]	D_{is} [m^2/s]	Pe	k [m/s]
Luvisol (Inf21)	$8.0314*10^{-7}$	$1.0562*10^{-8}$	5.2767	$1.6230*10^{-15}$
Calc. Reg (Inf23)	$7.3538*10^{-7}$	$7.8966*10^{-9}$	5.9169	$1.2784*10^{-9}$

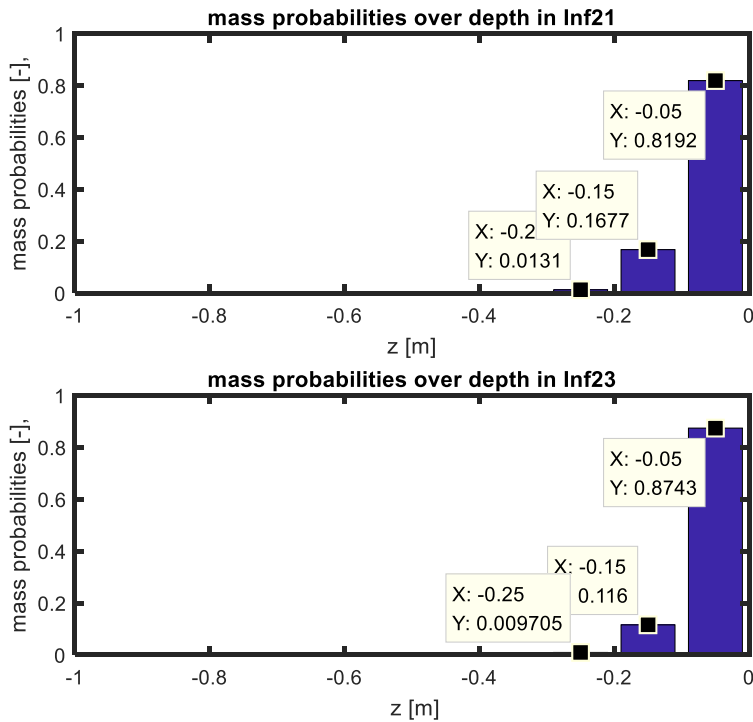Fig.3.2 Normalized Concentration Profile Over Depth of Inf21 and Inf23

Fig.3.3 Mass Probability Over Depth of Inf21 and Inf23

3.1.4 Simulated and observed normalized concentration

C) Simulate the tracer experiments assuming steady-state conditions and a constant, uniform moisture content equal to the initial value the analytical solution of the convection-dispersion equation. Compare the simulated and observed normalized

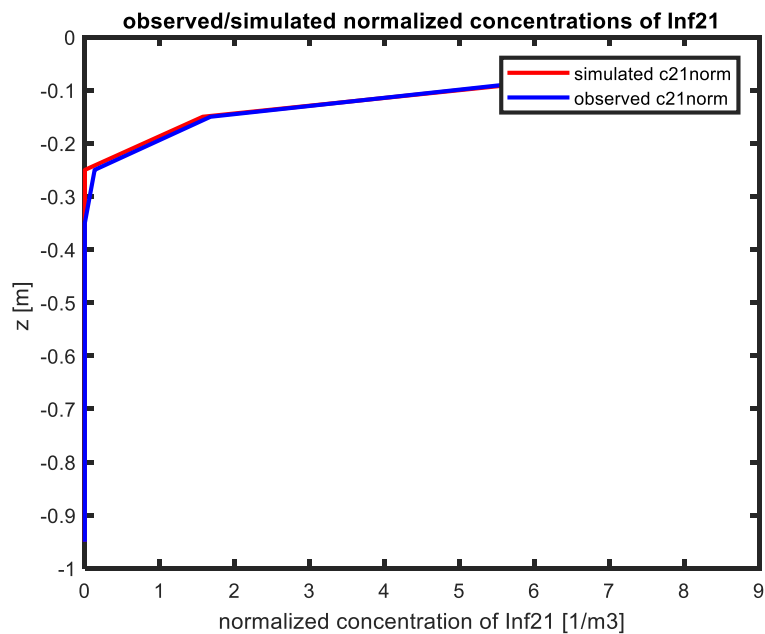concentration profiles. Use the MATLAB file "methods_of_moments.m" for this purpose.

Fig.3.4 Observed and Simulated Normalized Concentration of Inf21
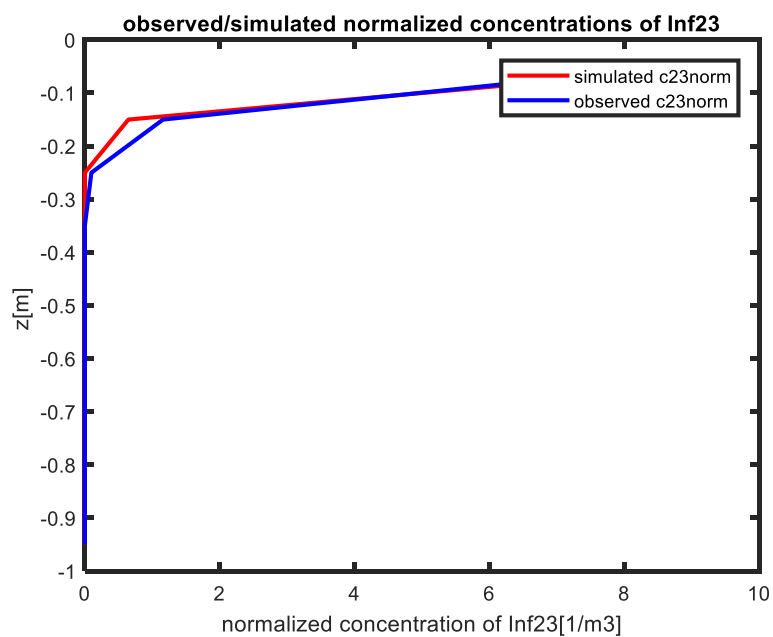

Fig.3.5 Observed and Simulated Normalized Concentration of Inf23

3.1.5 Validity of analysis

D) Discuss the validity of your analysis. What would you ideally need to assure that transport at these sites is in the well-mixed convective-dispersive regime?

According to Peclet number Pe listed in Tab.2, 5.2767 and 5.9169 for Inf21 and Inf23 respectively, we could assure that the values are much higher than 2, so the dispersion can be described as a well-mixed case.

3.2 Task2 Assess mobility and persistence of herbicides in typical soils of a rural catchment

In the mid-90s, the following herbicides were frequently used in the Weiherbach catchment: Isoproturon, Atrazine, Simazine, Terbuthylazine, Pendimethalin, Metamitron, Bromoxynil. The PPDB database provides the necessary data to judge the mobility and of these herbicides. These data were collected at many different locations in Europe, hence, the parameters were not unique but cover certain ranges.

3.2.1 Properties of herbicides

A) Select two herbicides and give a short characterization of the chemical and physical properties.

In this project, Simazine and Atrazine are selected as targeted herbicides. Their brief characteristics in terms of chemical and physical properties are presented in Tab.3.
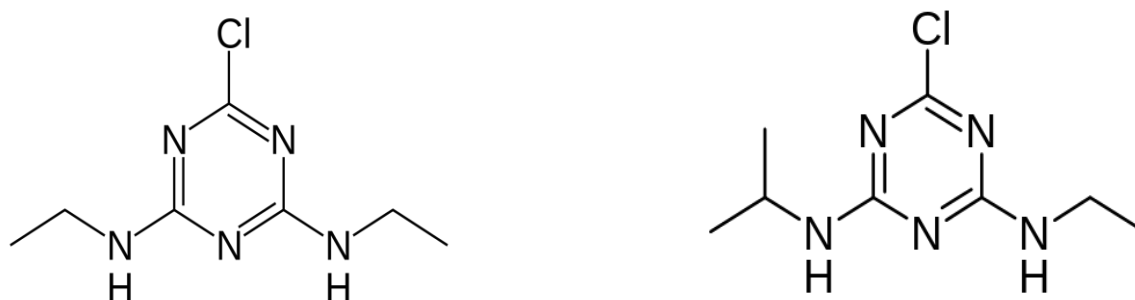

Fig.3.6 Chemical Structure of Simazine(left) and Atrazine(right)

Tab.3 Characteristics of Simazine and Atrazine [11, 12]

	Property	Simazine	Atrazine
Chemical Property	chemical formula	$C_7H_{12}ClN_5$	$C_8H_{14}ClN_5$
	molecular mass (g/mol)	201.66	215.68
Physical Property	solubility in water at 20 ℃ (mg/L)	5	35
	degradation point (℃)	226	/
	Kow at pH=7, 20 ℃	200	501
	bulk density (g/mL)/ specific gravity	1.3	1.23
	pKa at 25 ℃	1.62	1.7
	vapor pressure at 25 ºC (mPa)	0.00081	0.039
Degradation (aerobic) (DT50, days)	soil	60(typical), 90(field)	75(typical), 66(lab), 29(field)
	water-sediment	33	80
	water phase only	46	/
Linear Adsorption	Kd	/	/
	Koc	130	100
Freundlich Adsorption	Kf (mL/g)	15.88 (4.59-20.6)	3.2 (1.3-6.3)
	Kfoc	750	174
	1/n	0.76 (0.33-0.89)	1.07 (1.04-1.10)

3.2.2 Application of herbicides

B) Report their purpose, their application amount and usual application time (when provided).

1) Simazine, as a soil-acting non-selective herbicide, is used to control most germinating annual grasses and broad-leaved weeds. It has also been used to control algae in pond and fish hatcheries. It acts by inhibiting photosynthesis and remains active in the soil for 2 to 7 months or longer after application. But now it's banned in the European Union states.

Example applications are fruits, including berries, currants, apples, pears; hops; almonds; vines; canola; chickpeas; beans; lupins.

2) Atrazine is used to prevent pre- and postemergence broad-leaves weeds in crops such as maize (corn) and sugarcane and on turfs, such as golf courses and residential lawns.

It is one of the most widely used herbicides in USA and Australia agriculture, but it had no EU approval for use since 2003. It is volatile and, based on its physicochemical properties, there is a concern that it could leach into groundwater. It is generally not persistent in the field nor in an aquatic system. It is moderately toxic to mammals and most aquatic life, earthworms and honeybees but presents less risk to birds.

3.2.3 Freundlich isotherms

C) Calculate and plot the Freundlich isotherms for small concentrations up to the maximum concentration of the herbicide using the MATLAB file "Freundlich_isotherm.m". Explain how you deal with the parameter ranges of KF and 1/n (which corresponds to beta in our lecture notes). Calculate and plot the retardation coefficients.

In Fig.3.7 and Fig.3.8, Freundlich Isotherms in normal (0 to maximum solubility) and low concentration (0 to 1% of maximum solubility) conditions of two herbicides at different Kf values are all plotted.
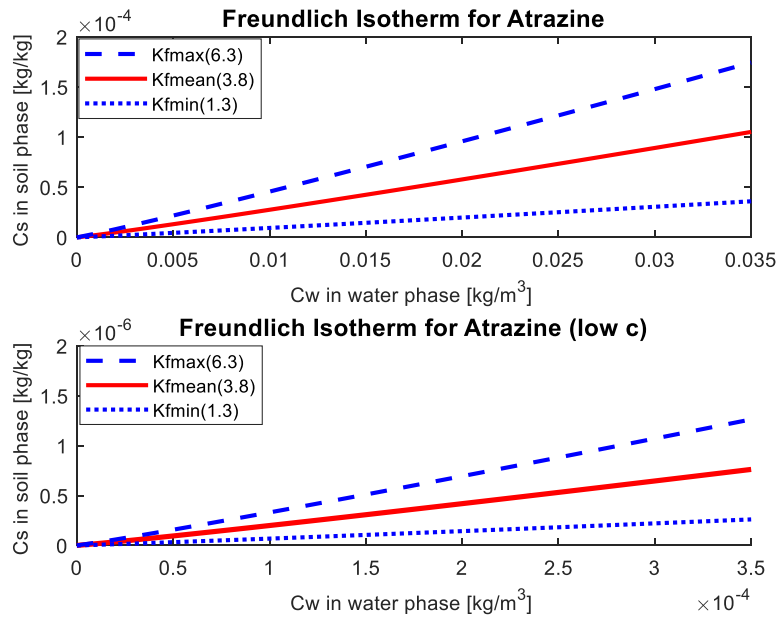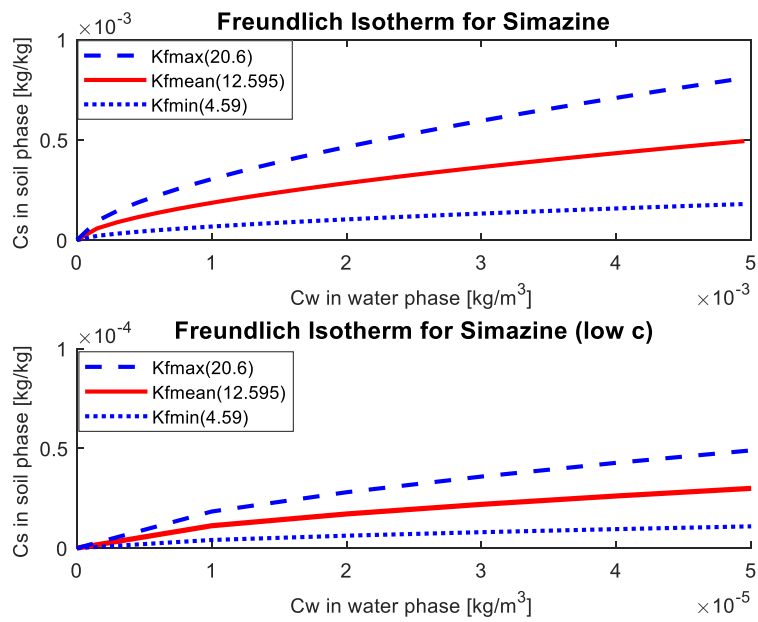
Fig.3.7 Freundlich Isotherm for Atrazine
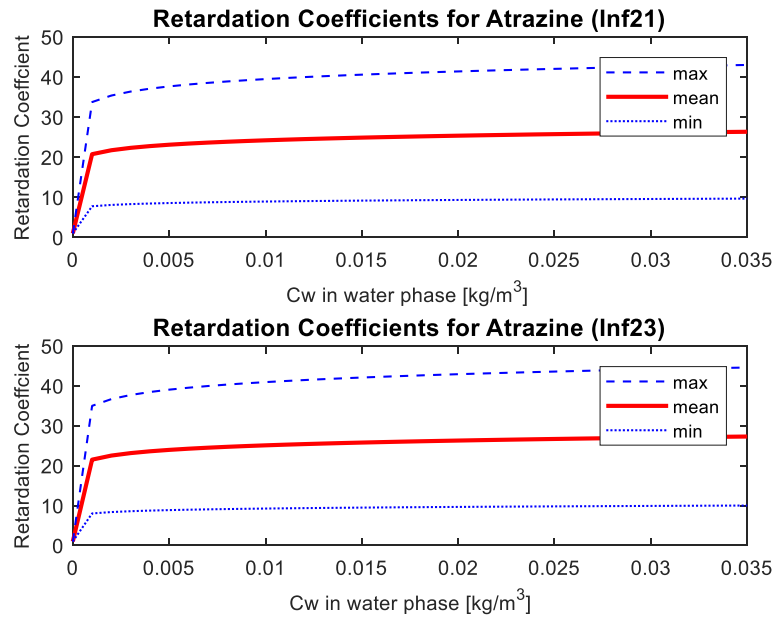

Fig.3.8 Freundlich Isotherm for Simazine

Fig.3.9 Retardation Coefficients of Atrazine in Inf21 and Inf23
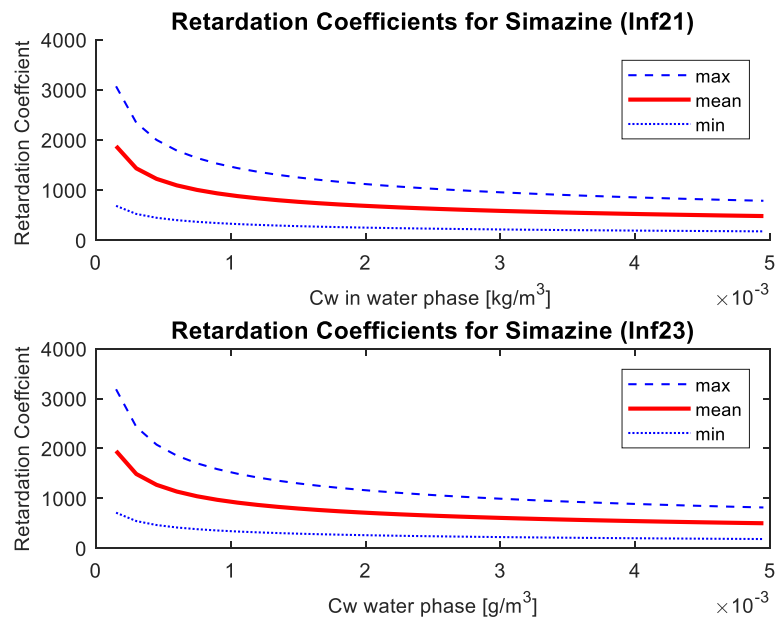

Fig.3.10 Retardation Coefficients of Simazine in Inf21 and Inf23

3.2.4 Kd value and retardation coefficient

D) Estimate the Kd value for the case of low concentrations for the selected isotherms (1% of the maximum concentration in the water phase) and calculate the retardation coefficients.

To calculate the maximum concentration in the water phase for each herbicide, the solubility at 20 °C was used.

Tab.4 Kd and R Values of Simazine and Atrazine

Herbicide	Soil (Site)	Kf (mean)	β	Kd			R		
				min	mean	max	min	mean	max
Simazine	Luvisol (Inf21)	12.6	0.61	0.2076	0.5697	0.9318	1636.4	4488.4	7340.5
	Calc.Reg (Inf23)						1698.4	4658.8	7619.1
Atrazine	Luvisol (Inf21)	3.8	1.07	0.00075	0.022	0.036	6.9214	18.309	29.6961
	Calc.Reg (Inf23)						7.1462	18.966	30.7854

3.2.5 Analytical transport model

E) Use the analytical model "Analytical_transport_model.m "and simulate leaching of your herbicides for your selected sites for low concentrations. Assume constant retardation factors (use the best and the worst case). Assume steady state flow conditions i.e. use the average transport velocity and dispersion coefficients from task 1.

Since there were 2 sites (Inf21 and Inf23), 2 herbicides (Atrazine and Simazine), 2 cases (best and worst cases), 2 decay situations (with or without decay), 16 unit situations will be separately considered.

In the simulation, best and worst cases use maximum and minimum retardation coefficients respectively. Transport time tc being equal to n*DT50 with n=0.5, 1, 2, 5 were all modeled.
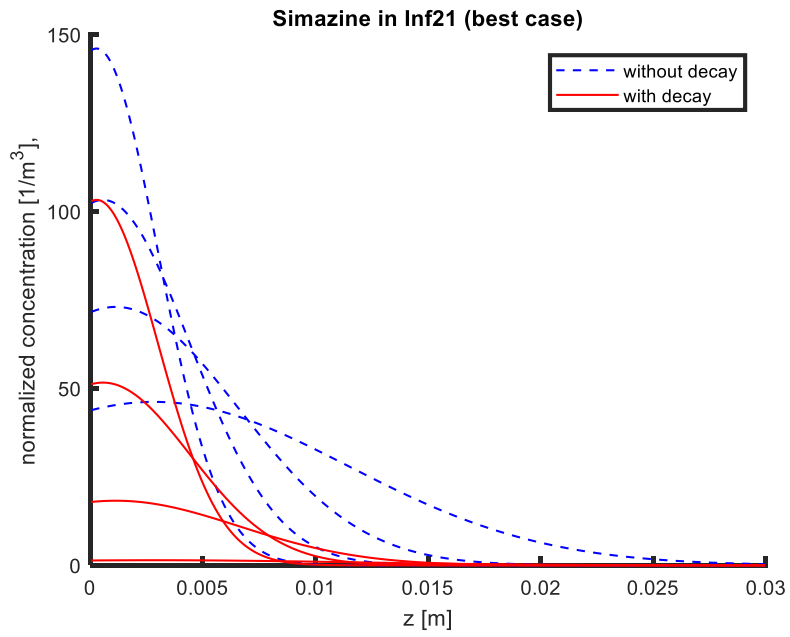
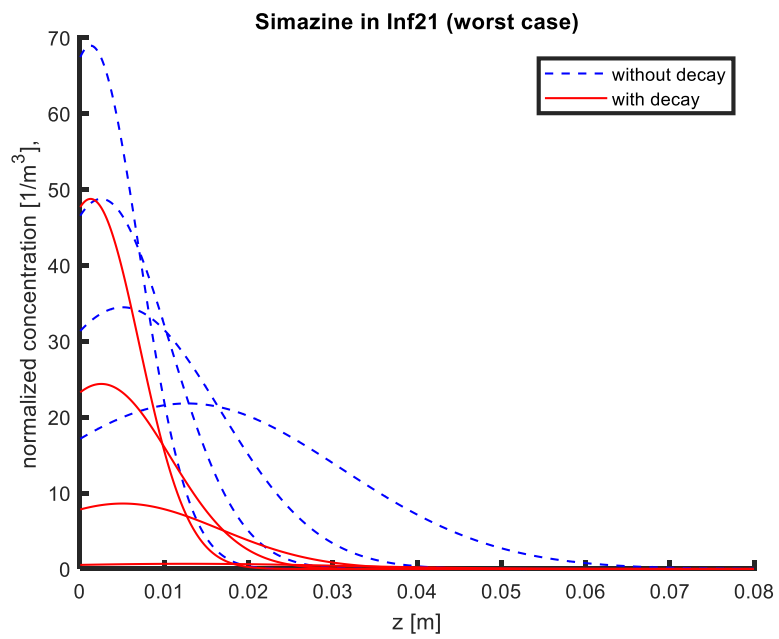Fig.3.11 Leaching of Simazine in Inf21 (best case)

Fig.3.12 Leaching of Simazine in Inf21 (worst case)
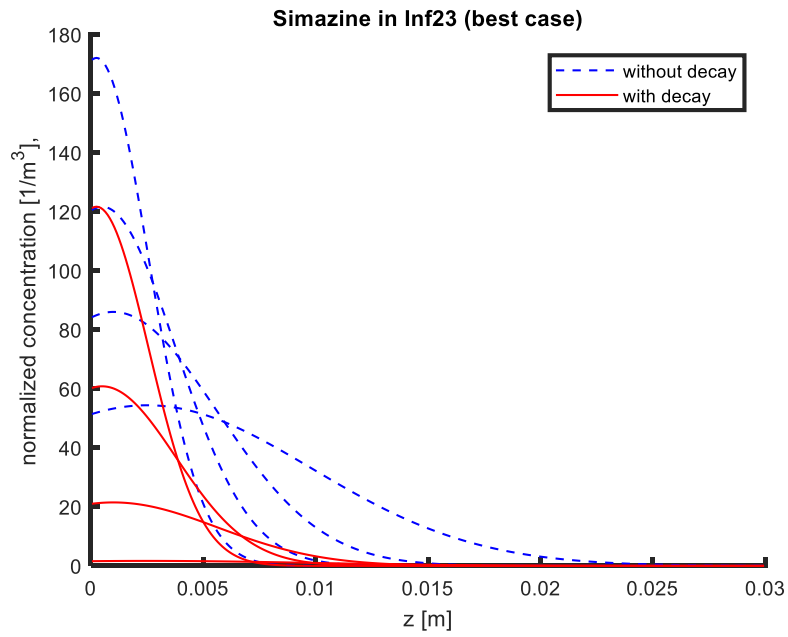
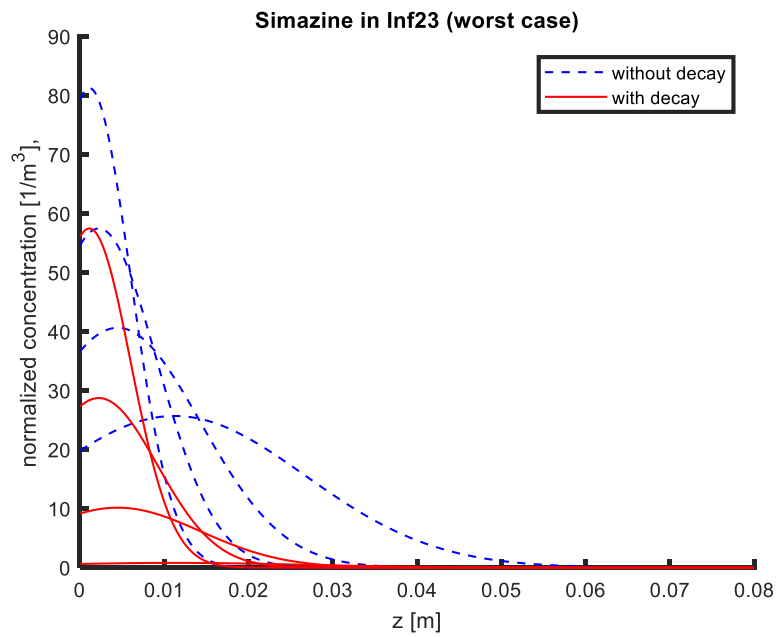Fig.3.13 Leaching of Simazine in Inf23 (best case)

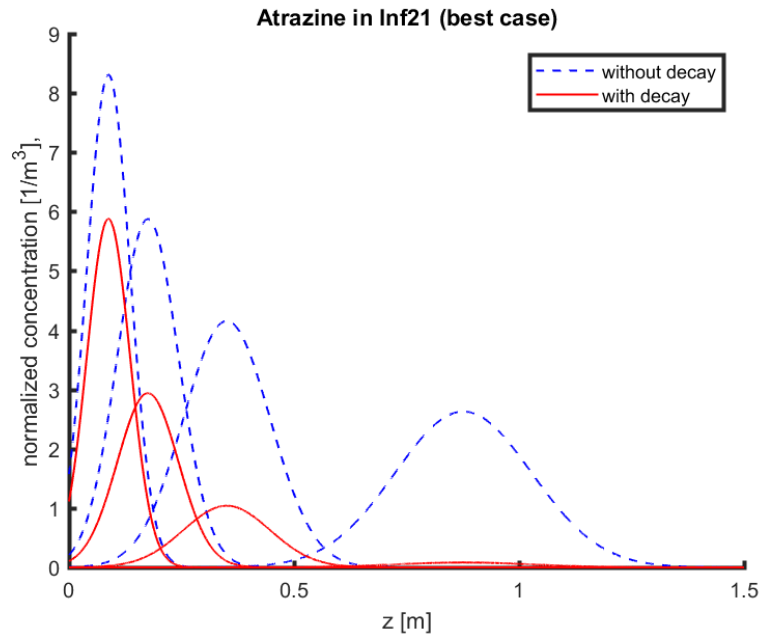Fig.3.14 Leaching of Simazine in Inf23 (worst case)

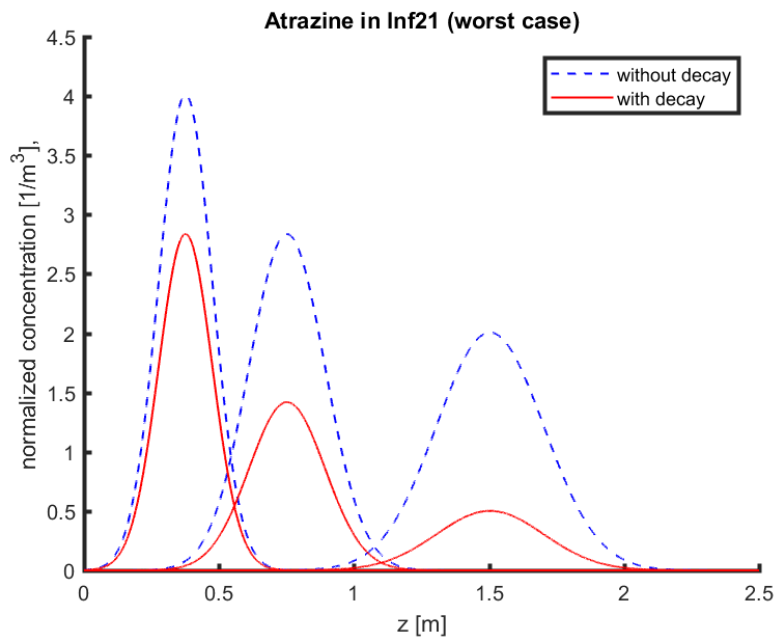Fig.3.15 Leaching of Atrazine in Inf21 (best case)

Fig.3.16 Leaching of Atrazine in Inf21 (worst case)
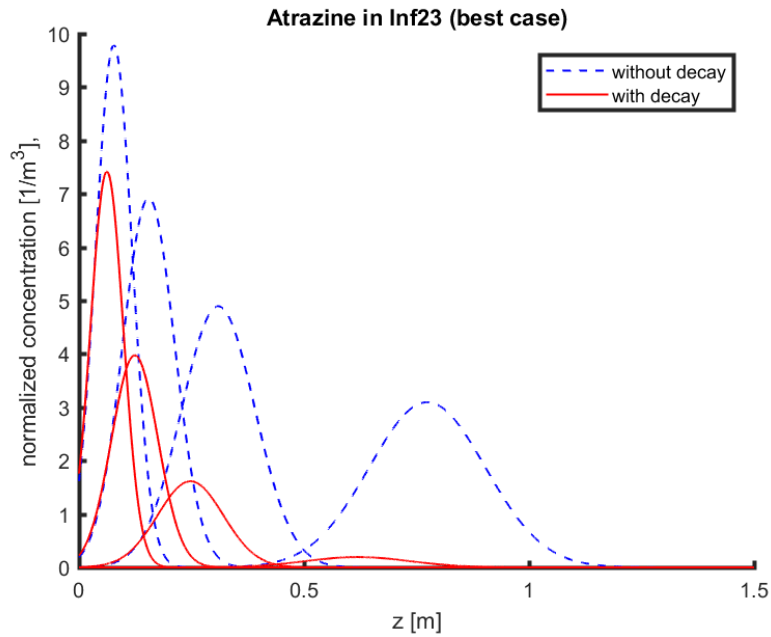
Fig.3.17 Leaching of Atrazine in Inf23 (best case)

Fig.3.18 Leaching of Atrazine in Inf23 (worst case)

3.2.6 Amount of herbicide that traveled into 1m depth

F) Include first order decay based on the DT50, which is the time after 50 % of the herbicide has been degraded (calculate the degradation constant from the DT 50 value). Discuss concentration profiles and the amount of the herbicide that traveled into 1m depth after a time t = n*DT50 for n= 0.5, 1, 2, 5.

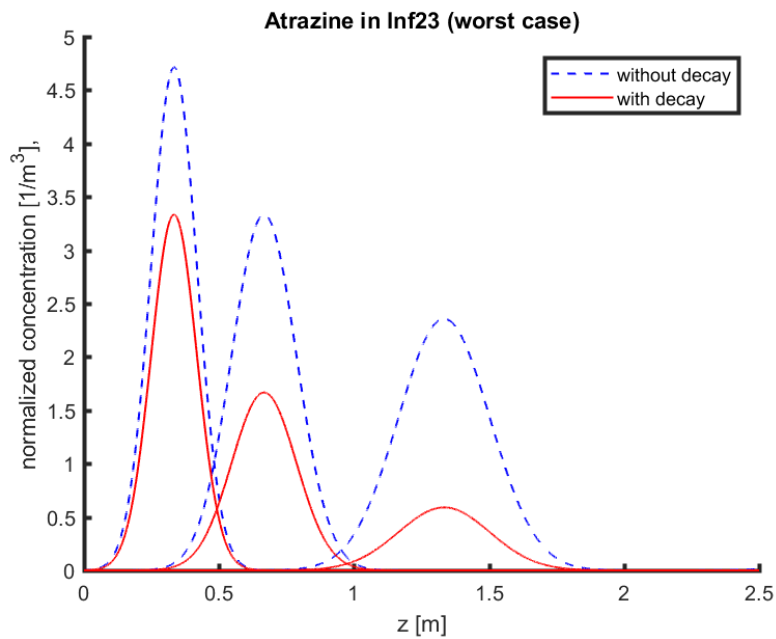Due to the fact of 2 sites, 2 herbicides, 2 cases (best and worst case), there were 8 unit situations. But according to the eight Figures shown before, only Atrazine passed more than 1 m, so there are only 4 cases left.

Tab.5 Amount of Atrazine at 1 m $[1/m^2]$

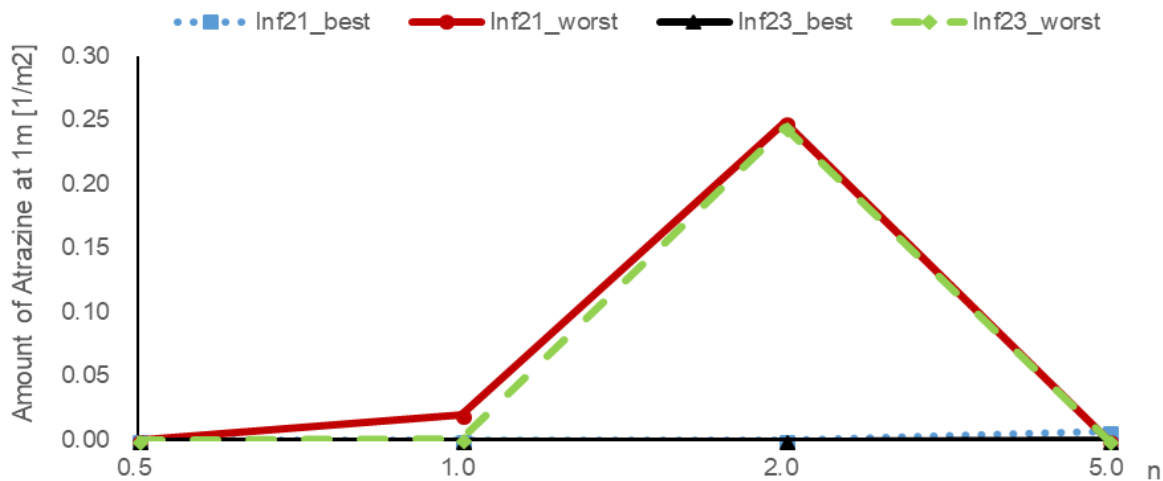| Site	Case	n			
		0.5	1	2	5
Inf21	best	0.0000	0.0000	0.0000	0.0065
	worst	0.0000	0.0194	0.2486	0.0000
Inf23	best	0.0000	0.0000	0.0000	$6.50*10^{-7}$
	worst	0.0000	0.0013	0.2439	0.0000

Fig.3.19 Amount of Atrazine at 1m

4 Conclusion and discussion

4.1 Task1

A) According to Fig.3.1, site Inf21 and Inf23 shared similar concentration range over depth and length (0 to 0.023 g/kg) and the concentration started to remain zero below -0.3 m depth. On the other hand, the concentration fluctuated less in Inf21 from 0 to -0.2 m than that in Inf23, as it was apparently higher in larger length and depth ranges in Inf23.

B) According to Tab.2, the average transport velocity $\bar{v}$ of tracer and the dispersion coefficient D_{is} of Inf21 were both slightly larger than those of Inf23. The Peclet

number Pe for Inf21 was slightly lower and this means that dispersion played a slightly more important role in Inf21. Additionally, Inf23 had a much lower hydraulic conductivity k even though k remained really small for both sites.

The normalized concentration of two sites followed the similar pattern, decreasing slowly from surface to deeper soil and remaining 0 since -0.4 m. The difference was that the normalized concentration was always a little higher in Inf23 at the same depth.

The mass probability, the mass portion at a certain depth in total mass, was also calculated and plotted and it proved the normalized concentration profile to a certain extent.

C) Fig.3.4 and Fig.3.5 illustrate the observed and simulated normalized concentration of Inf21 and Inf23. For Inf21, two curves were almost overlapped, which means the simulation or the measurement was really accurate. For Inf23, two curves overlapped except between the depth of -0.15 m to -0.25 m where the measured values are apparently higher.

4.2 Task2

C, D) For Atrazine, the Freundlich Isotherm curves were almost linear in both concentration conditions due to the fact that the beta value of Atrazine is 1.07, close to 1.

For Simazine, the Freundlich Isotherm curves are not so linear as Atrazine. We could see that in lower concentration range for both concentration conditions, the slope was generally much higher than that in higher concentration parts.

The retardation coefficients of Atrazine in Inf21 and Inf23 seemed similarly abnormal as the beta value of Atrazine was strangely larger than 1, which made the retardation coefficient at the concentration of 0 was always infinitely close to 1 and then the value started to increase dramatically in low concentration ranges and remained almost constant around 10, 28, 45 for minimal, mean and maximum Kf values respectively later. However, the difference of retardation coefficient between two sites was not obvious.

The retardation coefficients of Simazine in Inf21 and Inf23 were incredibly large up to around 800, 2000, 3000 for minimal, mean and maximum Kf values respectively.

These values drop quickly at low concentrations around 0.3 g/m^3 and then decreased slowly. Similarly, the difference of retardation coefficient between two sites was small.

Comparing Fig.3.9 to 3.10, the retardation coefficient changing trends were the same in Inf21 and Inf23 not matter for Simazine and Atrazine, in that the soil moisture values of two sites were close, being 0.179 and 0.159 m³/m³ respectively.

E) Simazine in Inf21 and Inf23 only transported approximately 0.03 m from larger concentration in the best case while in the worst case it can transport 0.08 m with smaller start concentration, which implied the influence of retardation effect. Also, the mobility of Simazine in Inf21 was slightly higher than Inf23 based on the maximum traveled depth. What's more, decay made concentration drop faster in near-surface depths maybe due to the stronger aerobic degradation of microorganisms. Without decay, there were slight increases of the concentration of Simazine in shallow soils.

Atrazine in Inf21 and Inf23 transports approximately 1.5 m in the best case while in the worst case it can transport 2.5 m, which also shows the influence of retardation effect. Similar to Simazine, the mobility of Atrazine in Inf21 is slightly higher than Inf23 based on the maximum traveled depth. The concentration of Atrazine fluctuated across the depth but always stayed lower level with decay.

F) In worst cases, with traveling time t=n* DT50 increasing from n=0.5, 1, the amount of herbicide Atrazine increased slowly, while greatly gained from n=1 to 2, reaching a high quantity level and then dramatically drops to roughly zero at n=5. Therefore, traveling time of Atrazine in soil should be avoided around 150 days.

In the best case, the amount of Atrazine seemed to remain constant around zero whatever the n is, which means retardation and degradation functioned well.

Last but not least, quoting the advice towards herbicides and pesticides given by the director of Holland's Plant Protection Service, practical advice should be "spray as little as you possibly can" rather than "spray to the limit of your capacity". Meanwhile, it is not sensible to "put poisonous and biologically potent chemicals indiscriminately into the hands of persons largely or wholly ignorant of their potentials for harm [Rachel Carson, 1962, Silent Spring]". Therefore, compreshensive reseach always needs to be developed before herbicides application.

5 Appendix

5.1 Text

1) cinf21.txt

2) cinf23.txt

5.2 MATLAB code

1) TASK1.m

2) TASK2.m

5.3 Figures

5.4 Tables

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